

Chapter 1

The Principles of Soil Testing

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Soil testing is practiced, with some degree of success, in nearly all parts of the world. Success or failure of soil testing varies depending upon the amount and quality of research data available for the calibration and interpretation of the tests. In some areas, agronomists are not entirely satisfied with the reliability or usefulness of soil tests. Quite often this lack of confidence may be traced to expectations that exceed the capability limits of the program. Many misconceptions seem to prevail as to just what soil tests can or cannot do. This chapter includes the realities and principles that form a general philosophy of soil testing.

Soil testing may be generally defined as any chemical or physical measurement that is made on a soil. But through common usage, the term *soil testing* has been given both a more restricted and broader meaning. The term is restricted in the sense that it has come to mean rapid chemical analyses to assess the plant-available nutrient status, salinity and elemental toxicity of a soil. It has broadened to represent a program that includes interpretations, evaluations, fertilizer, and amendment recommendations based on results of chemical analyses and on several other considerations. It is necessary, therefore, to distinguish between those factors that represent technical data and those that are interpretive judgments.

Sixteen elements are essential for crop growth. Three of these elements—N, P, and K—are commonly deficient in soil. Soil pH and salinity also commonly limit plant growth. Secondary and micronutrient deficiencies are found in some soils, with S, Zn, Fe, and B being the most common, but these are usually restricted to special soil areas. Therefore, soil testing predominantly involves N, P, K, and pH with salinity, but secondary and micronutrient analyses vary widely on a regional basis. Farmer acceptance of soil testing strongly depends upon the extent and severity of the limits for crop production, whether the problems are cost effectively treatable and the accuracy with which the tests can be used to predict crop responses with fertilizer and reclamation needs.

The nutrient status of a soil may be evaluated in several ways. Among these methods are (i) field-plot fertilizer trials, (ii) greenhouse pot experiments, (iii) crop symptoms, (iv) plant analysis, (v) rapid tissue or sap analyses, (vi) biologic tests (i.e., growing microorganisms on the soil to detect a nutrient deficiency or toxicity), and (vii) rapid chemical analyses of the soil. Each of these methods has certain limits when applied to individual farm fields or farms on a general service basis. Field-plot fertilizer trials are indispensable and serve as the basis from which the other diagnostic techniques derive a cause-and-effect relationship. However, fertilizer field trials, cannot, in a practical sense, be conducted on every farmer's field and the research results may not be directly transferred from one field to another, except for N in areas of high rainfall (> 75 cm/yr). A common transfer carrier is needed. Chemical analyses of the experimental soil and similar analyses of the soil to which the field-plot data are to be applied has proven useful and this is what "soil testing" is. Greenhouse fertilizer trials, besides being costly or time consuming, often give results that cannot be quantitatively extrapolated to the field. Deficiency and toxicity symptoms indicate only the very severe deficiency or toxicity condition. These symptoms usually appear too late in a growing season for a farmer to initiate remedial actions. Total plant analysis and plant sap analysis (rapid tissue tests) are postmortem types of analyses that help explain what was wrong that year on that soil but do not quantitatively predict fertilizer needs. Biologic tests can determine the nutrient status of a soil when properly conducted but are costly and time consuming. In summary, chemical analyses, or soil testing, can be rapid, inexpensive and accurate, and can serve as the transfer agent of field, greenhouse, and laboratory research into predictions of lime and fertilizer needs of a soil before crops are seeded.

Soil testing probably started, in some form or another, as soon as people became interested in how plants grow. The search for the "principle of vegetation" started long before, and actually led to, the development of the science of chemistry. One could classify Liebig (1840) as having been an early worker in the soil-testing field. Like many areas of agriculture, soil testing has had its followers and detractors. From Liebig's time in 1850, until the early 1920s, little progress was made. Dyer (1894), Hilgard (1911), and Burd (1918) made significant contributions to soil chemistry. During the late 1920s and early 1930s, significant contributions to soil testing were made by Bray (1929), Hester (1934), Morgan (1932), Spurway (1932), and Truog (1930). These workers understood the importance of measuring labile instead of total soil nutrient content. Since the late 1940s, soil testing has been widely accepted as an essential tool to formulate a sound lime and fertilizer program. Traditionally, soil testing has involved the evaluation of nutrient deficiencies in soils. Today, however, with the increased emphasis on environmental quality, soil tests are a logical tool to determine areas where adequate or excess fertilization has occurred. It is as important to determine where fertilizers should not be used as it is to determine fertilizer need. Currently, soil testing is used to evaluate salinity and elemental toxicity.

We cannot discuss the principles of soil testing without considering the objectives. Soil testing is an accurate and indispensable tool essential for the assessment of the fertility and productivity status of soils. To us the objectives of soil testing are to: (i) accurately determine the available nutrient status of soils, (ii) clearly indicate to the farmer the seriousness of any deficiency or excess that may exist in terms of the various crops, (iii) form the basis on which fertilizer needs are determined, and (iv) express the results in such a way that they permit an economic evaluation of the suggested fertilizer recommendations. The objectives recognize that soil test results per se are a part of the factual data and must, therefore, be reported in finite terms, while interpretations will vary with different crops and the resulting fertilizer recommendations will include interpretative judgments. Another objective of soil testing may be to identify soils (usually garden soils) with toxic levels of heavy metals leading to the production of unsafe vegetation for human and animal consumption or unsafe environments for work or play. In this chapter, we emphasize the former objective in agronomic production.

A sound soil-testing program requires an enormous amount of background research. This background research should determine, among other things, the significant chemical forms of the available nutrients in the soils of the area, the extractants most suitable for extracting all or part of the available nutrient forms, the relative productive capacity of the soils for the various crops, the differential response of the various rates and methods of fertilizer application for the different crops, field-sampling techniques, test procedures, and methodologies. The soundness of the required interpretive judgments will depend almost entirely on the thoroughness and quality of these background studies. Too often, especially in developing countries, soil-testing programs are started without an adequate research background. The chemical methods can be transferred easily from state to state, or country to country, but the research database required for valid interpretations and sound judgments usually cannot. As a result, soil-testing programs often flounder. We are not exaggerating when we say that the success of a soil-testing program is directly proportional to its research backing.

In most states, soil testing is a program that may be divided into four phases: collecting the soil samples, extracting and determining the index of soil fertility, interpreting the analytical results (indexes), and making the fertilizer recommendations. One should, therefore, speak of a soil-testing program and recognize that its success depends as much on good individual judgments as on accurate chemical analyses. Unfortunately, when errors are made the chemical analyses are the popular scapegoat.

In discussing in more detail the principles of soil testing, it is necessary, and more convenient, to do so on the basis of the various phases that comprise the program.

I. FIELD SAMPLING

The soil-testing program starts with the collection of a soil sample, or samples, from a field. The analytical results are expected to represent the

entire field. The first basic principle of the soil-testing program is that a field can be sampled in such a way that chemical analyses of collected samples will accurately reflect the field's true nutrient status. This does not mean that all of the samples must, or will, yield the same test results, but rather that the results reflect the true variations within the field. Differences of opinion exist as how best to sample a field to obtain an adequate evaluation of its nutrient level. This is because not enough research has been conducted in the area of soil sampling. Reuss et al. (1977) found that in eastern Colorado a systematic sampling plan was superior to a random one for $\text{NO}_3\text{-N}$. Also they discovered a large sampling error in the fields and the need for more intensive sampling. Depth of sampling is also important and should reflect the crop rooting system and nutrient distribution in soils. For mobile elements, deep samples should be taken. For example, Soltanpour et al. (1982) found that shallow (0–30 cm) soil samples were useless for predicting Se content of the dryland wheat (*Triticum aestivum* L.) grain from a soil test. But Se in deep (0–90 cm) samples correlated well with Se in grain. Although Se is not an essential plant nutrient, nevertheless the above example illustrates the importance of deep sampling under certain conditions. What must be recognized is that the entire soil-testing program can never be any more accurate than the accuracy of the soil sample or samples in characterizing the field. A single sample can seldom accurately characterize the nutrient status of a fertilized field.

In the past, before fertilizers were commonly used, it was relatively uncommon to find big differences in nutrient levels in different parts of a given field, except where extreme heterogeneity of soil types existed. Today, especially where fertilizers have been band applied, large differences are often found in the nutrient levels of samples taken from different parts of the same field. These differences usually are not sampling or testing errors but actual variations in fertility patterns. Wide test variations within a field pose the problem of determining or judging whether a single fertilizer recommendation can be prescribed for the entire field, or whether the variations are so great that different recommendations are required for different parts of the field. Sampling systems that were adequate for untreated soils will probably be inadequate for heavily fertilized fields. Many of our present sampling procedures will need to be reexamined, for the realities are, that fertilizer usage will continue, that variability in the fertility patterns within a given field will continue to grow, and that the problem of assessing the true, or average, fertility level for a given field will become more difficult.

II. EXTRACTION AND CHEMICAL ANALYSIS

Once the soil sample has been collected and prepared, the status of plant-available nutrients must be determined. By plant-available nutrient, one usually means the chemical form or forms of an essential plant nutrient in the soil whose variation in amount is reflected in variations in plant growth and yield. It is a basic principle of soil testing that simple rapid chemical analyti-

cal procedures can be designed to accurately measure, or be a measure of, the level of plant-available soil nutrients. The two parts for the laboratory analyses are extraction and measurement. Extraction involves the use of a chemical reagent solution to separate from the soil all or a fraction of the plant-available nutrient(s). Strict adherence to laboratory conditions, such as degree of soil pulverization, soil/solution ratio, and rate and length of shaking time are important because of the lack of an equilibrium between extracting solution and soil. Since the test value only has meaning in terms of plant response, should two soil test laboratories, testing the same soil sample and using the same extractant find different results, conditions of soil drying, pulverization, and extraction must be examined to reconcile the differences. Measurement is the determination of the amount of plant-available nutrient extracted. Any proven chemical analysis technique is acceptable. Here-to-fore extraction and measurement procedures have been dedicated to a single nutrient with each handling of a soil sample. In such systems, labor is the dominating cost of soil testing. With the advent of analytical instruments designed for multielement measurement, there is increasing research to develop multinutrient extractants. Several laboratories are already using such a system (Soltanpour, 1985). Many chemical methods have been suggested, and are being used, for the measurement of essential available plant nutrients. Actually, the chemical method used is important only to the extent that it must separate deficient from nondeficient soils and combined with other soil and plant variables predict fertilizer requirements of plants.

In working up and designing a chemical soil test, it is necessary to work with soil samples from fields of known crop response and which give a range in crop response. The method must show a mathematically definable increase in the measured plant-available nutrient as the indicated field crop response decreases. It is impossible to adequately correlate chemical soil test results with crop responses simply by testing large numbers of soils of unknown response. In the absence of soil samples from fields of known response, the chemical methods are correlated with greenhouse work using an index such as an "A-value" (Fried & Dean, 1952) or simply with response to a nutrient under greenhouse conditions. Alternatively, one may use a soil test proven useful in a different region with similar soils as a first approximation for finding a range of responding soils. While greenhouse and laboratory studies are useful in determining whether a method correlates with measuring plant-available form, it is important a method be calibrated with field response.

III. INTERPRETING THE ANALYTICAL RESULTS

Analytical results obtained from chemical analyses of soils must be interpreted meaningfully. This is usually accomplished through some type of a previously determined correlation between test results and known field crop responses. Methods that Cate and Nelson (1965), Nelson and Anderson (1977), and Kiesling and Mullinex (1979) developed can be used to develop the correlations. Therefore, valid correlation studies must precede intelligent interpre-

tations of soil test values. A basic principle of soil testing is that a soil test value can, under most circumstances, be treated and related as an independent variable to the percent yield and response obtained for a specific crop. Percent yield (yield of unfertilized crop as a percentage of fertilized crop) measures response to fertilizer under identical conditions of season, land, soil type, diseases, and weeds. Therefore, these latter variables are not required to be considered in interpreting the soil test. But, these variables are required to be considered for making a fertilizer recommendation specially for mobile nutrients.

At Illinois, the work of Bray (1944, 1945) has shown that the Mitscherlich equation, with minor modifications, can be used successfully to describe the yield associated with different levels of immobile available nutrients in the soil and different amounts of applied fertilizer.

IV. MAKING FERTILIZER RECOMMENDATIONS

In making a valid fertilizer recommendation, eight criteria must be known: (i) the soil test level of the soil, (ii) the crop to be grown, (iii) yield potential and percent sufficiency, (iv) the increase in yield with increasing rates of applied fertilizers, (v) the method of fertilizer application (i.e., banded vs. broadcast), (vi) leguminous crops preceding the crop to be grown in case of N recommendations, (vii) whether animal manure has recently been applied to the field and its potential contribution to nutrient status of the soil, and (viii) the degree of mineralization of native organic matter during plant growth, especially for N and S. Of these, the soil test simply indicates an index of the nutrient level in the soil. The soil test values say nothing about the yield potential of the soil, the season, the management practices, or the amount of fertilizer needed. The accuracy with which a test value can be interpreted will depend on the kind and quality of the field research work on which the correlations are based. The purpose of the soil test value is simply to indicate the starting point—the present level of available nutrients in the soil—on which the subsequent required judgments are based.

To interpret a soil test value, proper correlations of test values with known field responses for the various crops are required; that is, one must be able to determine and express the seriousness of the nutrient deficiency for a particular crop from the soil test value. In addition, crop response to different soil nutrient levels and to increased increments of both broadcast and band-applied fertilizer must be known. This factor requires considerable research, since it must involve combinations of different levels of available soil nutrients, different rates of applied fertilizers, different methods of applying the fertilizer, and different crops.

Economic considerations are important to determine the upper level of fertilization. This is especially true for the value of the expected crop increase as related to the cost of the fertilizer. To make these economic evaluations, an estimate is needed of the forthcoming yield of the particular crop and its probable value in absolute terms. This estimate is extremely difficult and

about the best one can do for any given year is to assume average yields and prices. The yield estimate will depend largely on the predetermined productive capacity of the soil, and some estimate of what constitutes an average yield in an average season under specified management systems. Therefore, all the factors used to determine the upper level of fertilization are based essentially on personal judgments. Once the upper level of fertilization for a crop has been decided, the actual amount of fertilizer needed to achieve that goal is the difference between the amount of available nutrients present (estimated from soil test value) and the amounts needed to achieve that upper limit. The amount of actual fertilizer needed is further modified by the method of applying the fertilizer (broadcast and banded), the efficiency with which increasing fertilizer increments have been shown to increase the yield and the kind of crop to be grown. Therefore, the final fertilizer recommendations depend on accurate soil test analyses and on interpretations of the test results based on sound research and judgment. An ideal method would be to recommend fertilizers for different yield levels and prices and allow farmers to choose the yield level and price combination they desire.

V. GENERAL SUMMARY

In a soil-testing program, as in any program, the results depend on the quality of the component parts. The primary objectives of the program are sound fertilizer recommendations for the various crops, yet many of our fertilizer recommendations are subject to criticism. Where then are the most probable sources of error?

The accuracy of most field-sampling techniques cannot be evaluated because of lack of extensive research data. Much greater variability in the fertility patterns of a field, as a result of band-applied fertilizers, may be expected. Additionally, sampling techniques, as well as interpretations of the results, must recognize irregular fertility patterns. Variations of test results within a field are not always because of faulty testing or sampling. They may present a true picture of the field's fertility patterns, which experience, past fertilizer history, and good judgment must reconcile in making the fertilizer recommendation.

Usually, the chemical analyses are the most accurate part of the soil-testing program in the sense that they are chemically reproducible on any given soil sample. Not all chemical methods measure the available form or forms of a nutrient in the soil. Errors are, therefore, more likely because of failure of the method to extract available-nutrient forms and to poor correlations than to the chemical reproducibility of the test.

Fertilizer recommendations depend on good fertilizer research directed towards determining the efficiency of different crops and soils of varying nutrient levels. If the results are expressed in terms of percent sufficiencies, the fertilizer recommendation needs only one personal judgment, that of picking the upper limit of fertilization. However, the selection of the upper limit may involve several judgments and usually depends on economic considera-

tions. The selected upper limit of fertilization may represent that point at which maximum returns per acre are expected: that point at which the last small increment of fertilizer used will give a yield increase just equal to the cost of the last fertilizer increment, or some lower point at which the value of the crop increases may be several times that of the fertilizer costs. Errors in these judgments include those of estimating the economics of expected yield increases in relation to the fertilizer costs, estimating the forthcoming season and the productivity capacity of the soil, evaluating the farmer managerial capacity, and many more. What users of soil testing must recognize is that every fertilizer recommendation is based on some individual's judgment as to what are reasonable expectations for a given situation, and that the expectation will probably not occur in any given year on any given field.

In all soil-testing programs, tables are prepared, or computer programs written, showing soil test results and suggested fertilizer use for various crops. However, judgments on which such tables are based are not always clearly indicated. What is often omitted in reporting soil test results is an indication of how serious the deficiencies are and the degree of response the farmer can expect if he carries out the recommendation. In fact, soil test results and accompanying fertilizer recommendations are almost always reported in such a manner that the farmer cannot evaluate them in terms of his own managerial and economic capabilities. This makes it extremely difficult for either farmers or field people to modify the average judgments used in such tables, or computerized programs, to accommodate their evaluation of the particular local condition.

A good soil-testing program is essential to sound fertilizer use. The soil test value is the starting point. It can indicate how serious the deficiency is and provide an anchor on which many of the subsequent required judgments depend. If a soil test value can be treated or expressed as an independent variable, fewer personal judgments are required and more accurate fertilizer recommendations will be made.

Currently, few soils being farmed do not require efficient fertilizer usage and good management for profitable crop production. On many soils, excess fertilizers are being applied and environmental concerns are being voiced. A sound soil-testing program is today's best and perhaps only way of determining what constitutes adequate, but not excessive, fertilizer use for high and efficient crop production.

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Chapter 2

Physical-Chemical Aspects of Nutrient Availability¹

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The instantaneous rate of nutrient uptake by a plant root is generally considered to be a function of the concentration of the dissolved absorbable form(s) of the nutrient at the root surface. Nutrient uptake models have used linear (Nye & Tinker, 1977) or Michaelis-Menten (Barber, 1984) equations to describe this function. Maintaining optimum plant growth over a growing season requires that a certain minimum concentration of the absorbable nutrient species be maintained at root surfaces to maintain required uptake rates. This requires transport from the bulk soil to the root surface to replace nutrients as they are absorbed.

The nutrient resupply system depends on a complex interaction of many chemical, physical, and biological reactions that can be visualized with the help of a comprehensive transport equation. If, for the sake of simplicity, we assume a one-dimensional flow system and select an infinitesimal volume of soil at a distance, x , from an actively absorbing plant root, the total flux, F , of dissolved nutrient toward the root is equal to the sum of convective and diffusive fluxes as shown in Eq. [1]:

$$F = vC_1 - (D_1 \theta f/b) dC_L/dx \quad [1]$$

where:

- v = velocity of water flow to the root, $\text{m}^3 (\text{soln}) \text{m}^{-2} (\text{soil}) \text{s}^{-1}$;
- C_1 = nutrient concentration in solution, $\text{mol m}^{-3} (\text{soln})$;
- C_L = labile nutrient concentration in soil, $\text{mol m}^{-3} (\text{soil})$;
- D_1 = diffusion coefficient of nutrient in solution, $\text{m}^2 (\text{soln}) \text{s}^{-1}$;
- θ = volumetric water fraction, $\text{m}^3 (\text{soln}) \text{m}^{-3} (\text{soil})$;
- f = conductivity factor related to path tortuosity, $\text{m}^2 (\text{soil}) \text{m}^{-2} (\text{soln})$; and
- b = buffer power = dC_L/dC_1 , $\text{m}^3 (\text{soln}) \text{m}^{-3} (\text{soil})$.

¹Contribution from the College of Agricultural and Life Sciences, Univ. of Wisconsin-Madison, Madison, WI 53706.

The negative sign in the diffusive flux term results from the fact that dC_L/dx is negative when flux is positive (flow is from high to low concentration). The term *labile* as used here refers to the amount of dissolved nutrient per unit volume of soil plus the amount of surface-bound nutrient per unit volume of soil that is in reasonably rapid equilibrium with the dissolved nutrient. The labile pool does not include nutrients present as precipitates except for those at the surface of the precipitate that react rapidly with the solution, nor does it include organic forms mineralized or immobilized by microorganisms. These forms are treated as separate source-sink terms in Eq. [2]. A source is defined here as any reaction that increases the concentration of a nutrient in the soil solution at a given point, and a sink is defined as any reaction that decreases the nutrient concentration at that point. Actually, the equilibrium between the labile-adsorbed and dissolved forms could also be treated as a source-sink reaction, but because these reactions are reasonably fast, they will be included in the diffusive transport term as a component of the buffer power.

A solute-conservation equation can be derived from Eq. [1] and the source-sink terms. If $D_1 \theta f/b$ and temperature are assumed constant, the equation can be written as:

$$(\partial C_L / \partial t)_x = v (\partial C_L / \partial x)_t - (D_1 \theta f / b) (\partial^2 C_L / \partial x^2)_t + (\partial C_p / \partial t)_x + (\partial C_O / \partial t)_x + (\partial C_V / \partial t)_x \quad [2]$$

where:

- C_p = nutrient in precipitates, mol m^{-3} (soil);
- C_O = nutrient in organic form, mol m^{-3} (soil);
- C_V = dissolved nutrient in potentially volatile form, mol m^{-3} (soil);
- x = distance from the root surface, m; and
- t = time.

When integrated using appropriate initial and boundary conditions, Eq. [2] can be used to calculate the concentration gradient away from the root as a function of time (Nye & Tinker, 1977). Because of the complexity of this differential equation, numerical methods are needed to solve it. However, this equation in its present form contains the various physical, chemical, and biological variables that affect the concentration and transport of specific nutrients and, therefore, will be used to focus the discussion that follows.

I. REACTIONS AFFECTING NUTRIENT AVAILABILITY TO ROOTS

A schematic representation of some important physical, chemical, and biological processes occurring in soils is shown in Fig. 2-1. The descriptions of these processes that follow are general in nature because the complexity of the soil system makes a rigorous theoretical approach to nutrient availability impractical given our present inability to define accurately the compo-

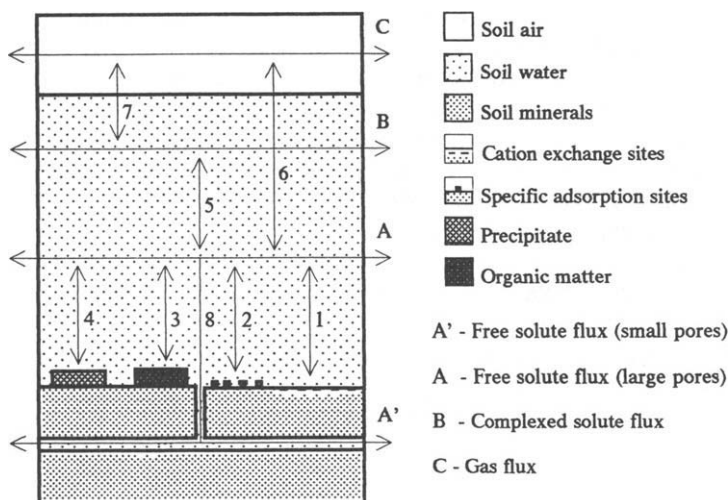


Fig. 2-1. Schematic representation of transport processes and source-sink reactions controlling solute transport in soil systems. Numbered reactions are as follows: (1) cation exchange, (2) specific adsorption, (3) precipitation/dissolution, (4) biological mobilization/immobilization, (5) complexation, (6) volatilization/solution of free solute, (7) volatilization/solution of complexed solute, (8) equilibration of solute between big and small pores. Oxidation/reduction reactions are not included in the figure, but they are important.

nents and properties of the system. Therefore, simple mathematical models of soil processes will be used in preference to more complex mechanistic models on the assumption that the coefficients of any model will have to be derived by curve fitting in a real-world soil system and that there is little improvement associated with the use of the more complex models. References giving more rigorous, theoretical treatments of the processes will be cited where appropriate. The two books of Sposito (1981, 1984) are particularly recommended for their comprehensive, rigorous coverage of the thermodynamics of soil solutions and surface reactions.

A. Complexation

Some plant nutrients, particularly the trace metals, form complexes (coordination compounds) with organic ligands (reaction 5 in Fig. 2-1). Chelates are complexes in which a metal ion acts as an acceptor of two or more electron-pairs donated by a single organic-ligand molecule. A single- or multiple-ring structure is formed, each ring consisting of the metal ion and usually four to six atoms from the ligand molecule. Some of these chelates are extremely stable, and the concentrations of strongly chelated metals, particularly Fe^{3+} and Cu^{2+} , can be many orders of magnitude greater than concentrations of free metal ions in soil solutions (Fujii et al., 1983). Chelating ligands usually carry a negative charge, but after reaction with the metal ion the charge may be negative, neutral, or positive depending on the initial negative charge of the ligand, the positive charge of the metal ion, and the num-

ber of H^+ ions displaced by the metal ion from electron-pair donor sites on the ligand. Positively charged chelates are not common in soil solutions because they are strongly adsorbed on soil cation-exchange sites. Chelate stability at constant metal-ion activity decreases with decreasing pH because of the tendency of H^+ to form electron-pair bonds with the ligand thereby displacing metal ions. However, if the activity of the metal ion is controlled by the solubility of a metal hydroxide, as with $Fe(OH)_3$, the increase in metal-ion activity with decreasing pH may more than offset the metal-displacing effect of the increasing H^+ activity.

Intact metal chelates do not appear to be absorbed by plant roots. Instead, the uptake rate seems to depend on the activity of the free metal ion at the root surface (Checkai et al., 1987). However, if equilibrium between free metal ion and chelate is approached at the root surface, the effective convective transport (first term in Eq. [1]) to the root will be a function of the total dissolved metal concentration rather than the free-ion concentration. This will also be true for the buffer power, b , in the diffusive transport term (second term in Eq. [1]). In both cases, the presence of the chelating ligand results in a greater transport rate than would be found with the existing free-ion concentration but no chelate. Chelation is particularly important in transporting nutrient metals of low solubility such as Fe. In fact, Fe-stressed plants have been reported to release Fe-complexing ligands into the soil solution to promote transport to the root (Romheld & Marschner, 1986). Other chelating agents such as citrate are common in rhizosphere soil (Marschner, 1986).

Addition of a chelating agent does not always result in increased availability of the chelated metals. In fact, adding chelating ligands can significantly lower free-metal-ion activities in the soil solution if those activities are not buffered sufficiently by labile solid-phase metals. Free-metal-ion activities are especially sensitive to addition of chelating agents in solution cultures where no solid-phase buffering is present. The ultimate effect of chelates on availability in soils will depend on whether the increased rate of transport to the root offsets the decrease in free-metal-ion activity in the bulk soil solution.

Dissolved ion pairs and small-molecular-weight complexes (single electron-pair bonds) should also contribute to transport in the soil solution, but their effects on absorption across cell membranes have not been well defined.

B. Adsorption on Particle Surfaces

Adsorption reactions on particle surfaces take the form of cation exchange on negatively charged surface sites (or, more rarely, anion exchange on positively charged sites) and specific adsorption of cations on electron-pair donor sites or anions on electron-pair acceptor sites. Most specific-adsorption sites also have some electrostatic contribution to the bond, and some involve mainly multiple ionic bonds where steric factors determine specificity [e.g., K^+ "fixation" in collapsed vermiculties and in mica edge sites

(McLean & Watson, 1985)]. Cation-exchange and specific-adsorption reactions are shown as reactions 1 and 2, respectively, in Fig. 2-1.

Cation-exchange sites may be associated with silicate minerals, oxide/hydroxide minerals or organic matter. In the commonly occurring expanding 2:1 layer silicate minerals most of the charge arises from isomorphous substitution of cations of lower valence for cations of higher valence in the octahedral or tetrahedral layers within the mineral. At the broken edges of silicate minerals or the surfaces of oxide/hydroxide minerals, fractional charges may be associated with electron-pair sites on surface oxygen ions. On organic matter, negative charge results when protons dissociate from surface weak-acid functional groups, primarily carboxyls and phenols.

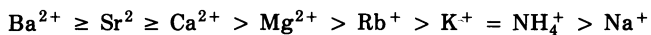
Charges arising from isomorphous substitution are insulated from the soil solution and are not affected by solution properties including pH. They are referred to as permanent charges. Charges arising at surfaces are affected by solution properties, particularly pH and specifically adsorbed ions. These are referred to as pH-dependent charges. At high pH, pH-dependent sites on mineral surfaces have fractional negative charges. As the pH decreases or the concentration of specifically adsorbed cations increases, H^+ or other specifically adsorbed cations will occupy some of the sites, and those sites will assume a partial positive charge. Therefore, as the pH decreases, the ratio of negative to positive charge sites decreases until a point of zero net charge is reached. Further decrease in pH will then produce a net positive charge on the surface. Alternatively, increasing pH or concentration of specifically adsorbed anions increases the ratio of negative to positive sites.

Association of H^+ with ionized weak-acid functional groups on organic matter changes the charge from -1 to 0 . Since there are no fractional charges on the organic matter sites and since additional protonation to a $+1$ charge does not occur in soil pH ranges, organic matter sites that are negatively charged at high pH do not become positively charged at low pH. However, organic matter does have N-containing functional groups such as amines in which the N has a free electron pair available for bonding H^+ (or other electron-pair acceptor). The protonated site would have a $+1$ charge. Based on pK values of about 9.2 for dissociation of the proton from NH_4^+ and 7.2 and 10.0 for dissociation of the two protons of protonated ethylenediamine (Sillen & Martell, 1964), one would expect that the amine groups on the organic matter should be protonated and have positive charges in the normal soil pH range. These positive charges are usually not noticed in soils, possibly because the positively charged amine groups are attracted to negative mineral sites and neutralized or are effectively neutralized by adjacent negative sites on the organic matter itself.

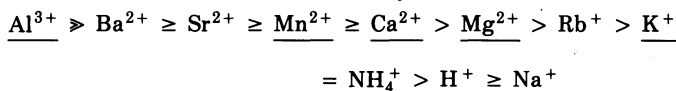
The attraction of cation-exchange sites for cations in solution increases with charge density and with nearness of the charge source to the particle surface. The relative strength of bonding of the individual cations depends on the force of attraction of the negative surface, the charge on the cation, the ionic strength of the solution, and the distance between the negative charge plane and the cation nucleus that depends on cation radius, hydration energy, and polarizability of the dehydrated cation. Generally, selectivity for a par-

Table 2-1. Relative strength of bonding of important exchangeable cations to cation exchange sites on planar surfaces of montmorillonite. (Order may differ somewhat on different exchangers). Cations normally present in significant amounts are underlined.

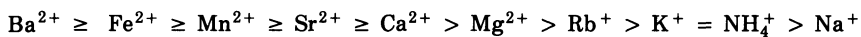
Slightly acid to alkaline soils:



Very acid soils:

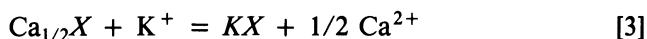


Neutral anaerobic soils:



ticular cation on cation-exchange sites is greater the higher the charge on the cation and, for cations of similar charge, the lower the hydration energy and the greater the polarizability. Because large cations bind water molecules less strongly than do small cations, there is a greater probability that a large cation can lose an associated water molecule and get closer to the particle surface than a hydrated smaller cation. However, if the attractive force is strong enough, the smaller cations may also be dehydrated and thus be preferentially adsorbed. Concentrating the soil solution (e.g., by evaporation) increases adsorption of ions of lower valence relative to those of higher valence in accord with the well-known ratio law (Schofield, 1947). Table 2-1 gives the usual strength-of-bonding order of cations normally found (or added with land-applied wastes) in soils that vary in pH and redox status. The proportions of the different cations found on the exchange will depend on relative solution activities as well as strength of bonding.

Several equations have been derived to describe the relationship between cation ratios in solution and on the exchange sites (Sposito, 1981, 1984). Most of them are similar for homovalent exchange but differ for heterovalent exchange. The Gapon equation is one of the simplest and will be used here to demonstrate the factors that affect the buffer power term in Eq. [2]. For more theoretically sound approaches, see Sposito (1981, 1984). The Gapon mass action equation for heterovalent cation exchange using the Ca^{2+} - K^{+} couple for illustration is given in Eq. [3] where X is a single negatively charged surface site:



The Gapon selectivity coefficient, K^G , is derived from this equation:

$$K^G = [\text{KX}] (\text{Ca}^{2+})^{1/2} / [\text{Ca}_{1/2}X] (\text{K}^{+}) \quad [4]$$

where [] denote concentrations and () activities.

In soils, each separate component that contributes to the cation-exchange capacity will likely have a different K^G . For the K^{+} - Ca^{2+} system, the rela-

tive affinity of the different sites for K probably increase in the order: organic < edge charge < smectites < vermiculite < mica edges. The K^G determined for a soil sample will be a weighted average of the K^G s of the individual components and will probably be valid only over a fairly narrow range of $(K^+)/ (Ca^{2+})^{1/2}$.

The effects of the variables in Eq. [4] on K activity are important because the K-uptake rate is a function of (K^+) at the root surface. These effects can be seen more clearly by solving Eq. [4] for (K^+) :

$$(K^+) = \{1/K^G\} \{[KX]/[Ca_{1/2}X]\} (Ca^{2+})^{1/2}. \quad [5]$$

This equation shows that the K activity in solution varies directly with the ratio of K to other cations on the exchange sites and the activities of competing ions (represented here by Ca^{2+}) in the soil solution, and inversely with the selectivity coefficient.

Because the total labile K per unit volume of soil is $[KX] + \theta[K^+]$, the K buffer power, b_K , can be calculated by substituting $\gamma_+[K]$ for (K^+) in Eq. [4] where γ_+ is the activity coefficient for K^+ , solving Eq. [4] for $[KX]$, adding $\theta[K^+]$ to both sides of the equation to convert the left side to labile K, and differentiating the labile K with respect to $[K^+]$.

$$\begin{aligned} b_K &= d\{[KX] + \theta[K^+]\}/d[K^+] \\ &= K^G \gamma_+[Ca_{1/2}X]/(Ca^{2+})^{1/2} + \theta. \end{aligned} \quad [6]$$

Thus, the K buffer power varies directly with the selectivity coefficient, the cation-exchange capacity not satisfied by K^+ , and the volumetric water content, and inversely with the activities of competing cations. If there is no adsorbed phase of a nutrient (as with NO_3^-) the buffer power is equal to the volumetric water fraction, θ .

Buffer powers for individual cations in complex mixtures normally found in soils can be calculated from solution concentrations and the exchangeable concentration of one of the cations if all of the competitive Gapon selectivity coefficients are known (Weitholter, 1983). However, any buffer-power values used in plant-uptake models should be derived using Gapon constants that are valid for the adsorption site mix and the solution composition of the soil in question. Effects of variation in solution composition over the growing season should also be considered.

In Tables 2-2 and 2-3, cations and anions, respectively, are grouped broadly according to relative selectivities on specific-adsorption sites. If a competitive Langmuir model (Veith & Sposito, 1977) is used, the mathematical derivation of buffer powers for nutrients that are specifically adsorbed is similar to that for the cation-exchange system. The major difference is the much greater range in selectivity exhibited by the specifically adsorbed nutrients. For example, results of Fujii et al. (1983) suggest that the selectivity coefficient for the Cd^{2+} - Ca^{2+} exchange on the most selective sites in soils is about 10^5 in favor of Cd^{2+} . However, as the Cd^{2+}/Ca^{2+} ratio in

Table 2-2. Relative strength of bonding of cations on complexing sites and on specific adsorption sites of minerals.

No bond	Weak	Strong
Na ⁺	Mg ²⁺	H ⁺ , Ag ⁺ , Al ³⁺
K ⁺	Ca ²⁺	Cd ²⁺ , Co ²⁺ , Cr ³⁺
NH ₄ ⁺	Mn ²⁺	Cu ⁺ , Cu ²⁺ , Fe ²⁺
Rb ⁺	Sr ²⁺	Fe ³⁺ , Hg ⁺ , Hg ²⁺
Cs ⁺	Ba ²⁺	Ni ²⁺ , Zn ²⁺ , Pb ²⁺

Table 2-3. Relative strength of bonding of anions on adsorption sites.

No bond	None to weak	Weak to moderate	Strong
NO ₃ ⁻	SO ₄ ²⁻	H ₂ BO ₃ ⁻	OH ⁻
Cl ⁻	SeO ₄ ²⁻	MoO ₄ ²⁻	H ₂ PO ₄ ⁻
	CrO ₄ ²⁻		H ₂ AsO ₄ ⁻
			AsO ₂ ⁻
			HSeO ₃ ⁻
			F ⁻

creases, the selective sites become saturated with Cd, and eventually Cd competes with Ca on cation-exchange sites where the selectivities are about equal (Hendrickson & Corey, 1981). The effect of pH is also more pronounced with specific adsorption reactions because H⁺ competes directly and strongly with specifically adsorbed cations for the sites and OH⁻ competes similarly with specifically adsorbed anions such as H₂PO₄⁻.

One potentially important factor affecting buffer power calculations for adsorption systems that is rarely mentioned in the literature is pore size. If a uniform surface-adsorption-site density is assumed, the ratio of surface-adsorption sites to volume in a cylindrical pore will be inversely proportional to the pore radius. Therefore, at a constant solution composition, which would maintain a constant fraction of the sites saturated with a given solute, the amount of adsorbed solute per unit volume of pore would also be inversely proportional to the pore radius. If the dissolved solute is insignificant compared with the amount adsorbed, as is frequently the case with strongly adsorbed solutes such as H₂PO₄⁻, the local buffer power will also be inversely proportional to the pore radius. This has a dramatic effect on the distance that a solute will diffuse in a given time because the mean-square diffusion distance at a given time is inversely proportional to the square root of the buffer power (Jost, 1960). This slow diffusive transport through small pores is shown as transport process A' in Fig. 2-1, and the equilibration of solute between large and small pores is shown as reaction 8.

C. Precipitation

Solubility-product criteria can control activities of plant nutrients that form precipitates in soils (reaction 3 in Fig. 2-1). If a plant nutrient tends to form a precipitate under soil conditions, the following sequence usually occurs in the precipitation process as the concentration of the nutrient in

Table 2-4. Common precipitates in soil systems (underlined) and other substances that can form similar precipitates or coprecipitates with the common precipitates.

Hydrous oxides	Carbonates	Phosphates	Sulfates	Sulfides
<u>Fe</u> ³⁺	Ba ²⁺	<u>Fe</u> ³⁺	<u>Ca</u> ²⁺	<u>Fe</u> ²⁺
<u>Al</u> ³⁺	<u>Ca</u> ²⁺	<u>Al</u> ³⁺	Ba ²⁺	Ag ⁺
Ca ²⁺	Cd ²⁺	<u>Ca</u> ²⁺	Hg ₂ ²⁺	As ³⁺
Co ²⁺	Co ²⁺	<u>Fe</u> ²⁺	Pb ²⁺	Cd ²⁺
Cr ³⁺	Cu ²⁺	Ag ⁺	Sr ²⁺	Co ²⁺
Cu ²⁺	Fe ²⁺	Ba ²⁺	SeO ₄ ²⁻	Cr ³⁺
Fe ²⁺	Hg ₂ ²⁺	Cd ²⁺		Cu ⁺
Hg ²⁺	Mg ²⁺	Co ²⁺		Cu ²⁺
Hg ₂ ²⁺	Mn ²⁺	Cr ³⁺		Hg ₂ ²⁺
Mn ²⁺	Ni ²⁺	Cu ²⁺		Hg ²⁺
Ni ²⁺	Pb ²⁺	Fe ²⁺		Mn ²⁺
Pb ²⁺	Sr ²⁺	Hg ₂ ²⁺		Ni ²⁺
VO ²⁺	Zn ²⁺	Mn ²⁺		Pb ²⁺
Zn ²⁺		Ni ²⁺		Sn ²⁺
		Pb ²⁺		Zn ²⁺
		Sr ²⁺		
		Zn ²⁺		
		AsO ₄ ³⁻		
		F ⁻		

the soil solution increases (Corey, 1981): (i) adsorption on particle surfaces, (ii) supersaturation with respect to the reactants in the precipitation reaction, (iii) nucleation of the precipitate on the particle surfaces, and (iv) crystal growth. It is only when the precipitate is present (stages 3 and 4) that the solubility product of the precipitation reaction controls the activities of the reacting species. Even then, significant undersaturation or supersaturation of reactants in the soil solution may occur if addition or loss of reactants occurs faster than the reattainment of equilibrium with the precipitate.

The major classes of precipitates found in soils are silicates, oxides, hydroxides, carbonates, phosphates, sulfates, and sulfides. Specific precipitates in these classes (except silicates) are listed in Table 2-4. The underlined elements in Table 2-4 form the common precipitates and the others are usually found as coprecipitated minor constituents within the major precipitates (Corey, 1981). Solubility products for most of the pure precipitates listed can be found in Lindsay (1979).

The coprecipitation process can best be illustrated with an example. Both Ca and Mn form carbonate precipitates. If Ca is present at relatively high concentration in the soil solution and Mn at relatively low concentration, and the CO₃²⁻ concentration is raised to the point that CaCO₃ starts to precipitate, Mn will be coprecipitated along with the Ca even though the solubility product of MnCO₃ is not exceeded. The ratio of Ca to Mn in the precipitate will depend on the ratio in solution and their relative affinities for surface adsorption during the crystal-growth process. If the ratio of

Ca^{2+} to Mn^{2+} remained constant and the ions were freely diffusible within the precipitate, the relationship between the ratio of ions in solution to the ratio in the precipitate could be described by a separation factor, D (Sposito, 1981):

$$D = [(\text{CaCO}_3)_s/(\text{MnCO}_3)_s]/[(\text{Mg}^{2+})/(\text{Ca}^{2+})] \quad [7]$$

where the parentheses around the two solid phases indicate activities of those phases which can be approximated by their mole fractions. However, if the Mn^{2+} concentration is not well buffered and the ions are not freely diffusible within the precipitate, the relative rate of Mn depletion from solution will differ from that of Ca so that the Ca/Mn ratio in solution will change continuously during precipitation, and the Ca/Mn ratio in the central part of the precipitate will differ from that at the surface. If equilibrium between the particle surface and the soil solution is ultimately attained, the solution activity of Ca, the major constituent, can be predicted quite accurately from solubility-product calculations, but this is not the case with Mn. It is generally true that solution activities of solutes that are minor constituents in solid solutions cannot be predicted accurately from precipitate composition and solubility product criteria (Garrels & Christ, 1965).

The rate at which nutrient ions are released from precipitates depends on the surface exposed and the rate-limiting step for dissolution (Sparks, 1987). The rate-limiting step may be the rate of detachment from the particle surface (surface control) or the rate of diffusion from the saturated solution at the particle surface to the bulk solution (diffusion control). For many precipitates, particularly those that form discrete crystals, the surface exposed is small relative to the concentration of potential adsorption sites for the precipitate constituents on soil-particle surfaces. For example, crystals of variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, might form in an acid soil. That soil would also contain potential P-adsorbing sites on edges of silicate minerals and on sesquioxide surfaces. The number of adsorbing sites per unit volume of soil would probably be orders of magnitude greater than the number of sites exposed on the surface of the variscite particles. If equilibrium were attained, the activity of P in solution would be controlled by the variscite solubility product, but the major source of buffering against rapid changes in P activity (the buffer power) would be the surface adsorption sites. Therefore, in Eq. [2], precipitation reactions are considered to be source-sink reactions within the infinitesimal soil volume, and the total labile forms, which include the precipitate surface, are assumed to be the labile solid-phase component of the buffer power.

An exception to the model of precipitates providing long-term solubility control of adsorbable/precipitable solutes and adsorbed phases providing the major short-term buffering can be found with the iron oxides. Iron oxide precipitates form coatings on particle surfaces and, indeed, are major adsorbing surfaces for many specifically adsorbed nutrients. According to

Lindsay (1979), this " $\text{Fe}(\text{OH})_3(\text{soil})$ " has a solubility product intermediate between that of amorphous $\text{Fe}(\text{OH})_3$ and $\gamma\text{Fe}_2\text{O}_3$, and, because of its large surface, it probably controls the Fe^{3+} activity in soils in the short term as well as the long term.

D. Mineralization and Immobilization by Organisms

For some plant nutrients such as N, S, B, and P, a major input to the labile pool is mineralization of organic matter containing significant concentrations of those nutrients. Conversely, some labile nutrients can be immobilized during the decomposition process by incorporation into microbial cells if the nutrient concentration in the organic material is not sufficient to meet the needs of the microorganism doing the decomposing. The details of these reactions are covered in numerous texts (e.g., Tate, 1987; Paul & Clark, 1989) and will not be discussed here. In Eq. [2], these reactions are considered to be source-sink reactions that do not contribute to buffer power because no equilibrium exists between solution and solid phases. Mineralization/immobilization rates are determined by the factors that affect the activities of the organisms involved.

E. Liquid-Gas Interactions

Some of the plant nutrients such as C, H, O, N, and S may exist in gaseous form in the soil. Under aerobic conditions, CO_2 , H_2O , O_2 , and N_2 are common constituents of the soil air. Under anaerobic conditions, CH_4 , H_2 , NO , N_2O , and H_2S may form and free O_2 may disappear. At high pH, volatilization of NH_3 may become significant.

The interchange between gaseous molecules in the soil air and those dissolved in the soil solution is governed, at low concentrations, by Henry's law. According to this law, the solubility of a gas in the soil solution is proportional to the partial pressure of the gas in the soil air. Volatile constituents can be transported relatively rapidly to the atmosphere if there is sufficient air permeability because diffusion coefficients in air are about 10^4 times those in water. Therefore, the rate of gas diffusion through soils depends on the number and continuity of air-filled pores which, in turn, are complex functions of the water content. The ability of gas diffusivity models to predict gaseous diffusion in soils is limited by the uncertainty of this relationship between gas permeability and water content (Collin & Rasmuson, 1988). Gaseous transport is represented by process C in Fig. 2-1, and the equilibrium between solution and gas phases is shown as reactions 6 and 7.

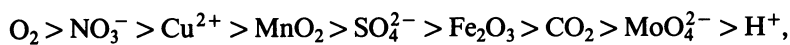
Reactions involving liquid-gas interchange are treated as source-sink reactions in Eq. [2] because many of them are microbially mediated and are not reversible.

F. Oxidation/Reduction (Redox)

Redox reactions involve the transfer of electrons. The redox potential is a measure of the tendency of an atom, ion, radical, or molecule to donate

or accept electrons. A high redox (reduction) potential indicates a strong tendency to accept electrons from an electron donor with lower redox potential. If the electron transfer occurs, the electron acceptor is converted from an oxidized to a reduced state and the electron donor is converted from a reduced to an oxidized state. Many substances remain in metastable redox states because the activation energy required to make the reaction proceed is not available and this prevents them from achieving thermodynamic equilibrium. In many of these cases, microbial enzymes can act as catalysts to make the reactions proceed to the equilibrium state.

In soil systems, the source of electrons that drives most redox reactions is the microbial respiration process. In respiration, electrons are transferred from C to an electron acceptor with the release of energy. If O_2 is available at the respiration site, it is the preferred electron acceptor because the greatest energy release is then obtained. If O_2 is not available, the organisms usually select the electron acceptor that gives the next greatest energy release, and this electron acceptor is reduced in the process (Harris, 1982). Based on the redox potentials as given by Lindsay (1979), the usual energy-release order of potential electron acceptors in soil systems at pH 7 is



with the underlined elements being the most important electron sinks. In aerobic soils, autotrophic bacteria may oxidize reduced forms of some of these nutrients to obtain energy using O_2 as the electron acceptor.

Redox reactions do not enter directly to Eq. [2] or Fig. 2-1, but they do affect many of the reactions shown there. Any time the rate of O_2 used in respiration exceeds the transport of O_2 to the respiration site, reduction of alternative electron acceptors proceeds. This results in a change in the chemical species of individual nutrients. In his Tables 13.3 and 13.4, Spósito (1989) distinguishes between plant-nutrient elements that are directly affected by changes in redox potential and those that are indirectly affected. Generally, those directly affected undergo changes in oxidation state in response to changes in the redox status, whereas those indirectly affected undergo changes in concentration or chemical species without a change in oxidation state. Nutrients indirectly affected include those that can be adsorbed or precipitated on Fe(III) or Mn(IV) hydroxy solids (released to the solution if the solid phase dissolves), those that form inorganic sulfides and those that compete with Fe^{2+} or Mn^{2+} for cation-exchange or specific-adsorption sites in reduced systems.

G. Plant Root Effects

Reactions at the root-soil interface affect the environment of the rhizosphere. The plant root is the ultimate sink for both nutrients and water in nutrient-uptake models. In addition to this function, the root changes the rhizosphere environment through exudation of CO_2 , H^+ , HCO_3^- and

organic compounds. The CO_2 is a product of root respiration, whereas H^+ and HCO_3^- are excreted to maintain electrical neutrality when the root absorbs more equivalents of cations than anions (H^+ release) or more equivalents of anions than cations (HCO_3^- release). The change in rhizosphere pH as a result of these excretions can be as much as 2 pH units (Marschner & Romheld, 1983). Rhizosphere pH changes of this magnitude have a marked effect on solubilities of many nutrients. A major factor determining whether H^+ or HCO_3^- will be excreted is whether N is taken up as NO_3^- (HCO_3^- release) or NH_4^+ (H^+ release) or fixed from atmospheric N_2 (H^+ release).

Organic compounds released by roots fall into three categories: low-molecular-weight compounds (free exudates), high-molecular-weight gelatinous compounds (mucigel), and sloughed-off tissues and their lysates (Marshner, 1986, p. 454). Some of the low-molecular-weight compounds are complexing agents, and some of the compounds of higher molecular weight exhibit cation-exchange and specific-adsorption sites. All of the compounds serve as C sources for microbial respiration and cause an increased O_2 demand in the rhizosphere compared with the bulk soil.

II. SUMMARY

Optimum nutrient availability to plants over a growing season requires an adequate sustained supply of absorbable forms of the essential nutrients at the root surface. This involves mobilization of nutrients from labile forms adsorbed on particle surfaces (exchangeable and specifically adsorbed forms), from dissolution of precipitates, or from mineralization of organic forms with subsequent transport to the roots via convection or diffusion. A solute-conservation equation was used to illustrate the reactions that would occur within an infinitesimal volume near an actively absorbing root. These include the transport processes, convection and diffusion, and the source-sink reactions of adsorption-desorption on cation-exchange and specific-adsorption sites, precipitation-dissolution, mineralization-immobilization of organic forms, and volatilization-solution across the air-water interface. Soluble complexed forms enhance transport even though they are not absorbed as such. Redox reactions change the kinds and amounts of dissolved and precipitated nutrient species in addition to affecting root respiration. Exudates from plant roots affect pH, concentration of complexing ligands, and oxygen demand in the rhizosphere. An understanding of how all of these reactions interact is needed in developing a nutrient-uptake model that can be applied over a variety of soil conditions. It is also helpful in designing soil-testing methods and interpreting their results.

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Chapter 3

Soil Sample Collection and Handling: Technique Based on Source and Degree of Field Variability

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The reproducibility, or analytical precision, of laboratory tests done on a composite sample from a field may be very high. However, the precision of tests on different samples from the same field is often very low. This is related to both vertical and horizontal variability in the field.

Field researchers have long been aware of soil heterogeneity (Waynick, 1918). Early researchers used an effective but time-consuming method to evaluate soil heterogeneity. This was known as the uniformity trial (LeClerc et al., 1962). The method was simply to plant a crop and manage it uniformly throughout the growing season. The field would be divided into small segments and crop yield measured on each segment. Crop yield variability among segments was taken as the measure of soil fertility heterogeneity in the field. The crop yield data obtained from a uniformity trial were plotted on a map, and field segments having similar yields were connected by smooth lines. This represented a soil fertility isoline or contour map. LeClerc et al. (1962) drew two general conclusions from the early uniformity trials:

1. Soil fertility variations are not distributed randomly, but they are, to some degree, systematic; that is, contiguous field segments are more likely to be alike than are segments separated by some distance.
2. Soil fertility is seldom distributed so systematically that it can be described by a mathematical formula.

The conclusions are equally valid today in describing the fundamental problems associated with soil sampling. Nowadays, soil fertility is most often estimated from chemical analyses of soil samples. Accordingly, soil sampling methodology must be critically evaluated to obtain an understanding of true field characteristics with respect to variability.

Some principles of soil sampling were outlined by Cline (1945) and reviewed by Petersen and Calvin (1965). These authors described the following soil sampling schemes: (i) simple random, (ii) stratified random, and (iii) systematic. They also showed methods of calculating the population means, variances, and confidence limits for the various sampling schemes.

The mean \bar{x} , variance S^2 , standard deviation (SD), and coefficient of variation (CV) are defined as follows:

$$\bar{x} = \Sigma x/n \qquad CV = SD/\bar{x}$$

$$S^2 = \{\Sigma x^2 - [(\Sigma x)^2/n]\}/(n - 1)$$

$$SD = \sqrt{S^2}$$

where n = number of individuals sampled.

Rigney and Reed (1945), Reed and Rigney (1947), and Jacob and Klute (1956) used components of S^2 among samples within an area, and S^2 among determinations on the same sample. In general, they concluded that differences between determinations on the same sample were small when compared to differences among samples. Another general conclusion was that different soil properties (e.g., pH, P, K, and lime requirement) had different patterns of variation. These workers also showed how to determine the best or most economical sampling scheme for any given field using estimates of S^2 obtained from previous work on the same field.

Beckett and Webster (1971) reviewed data on the lateral variability of soil properties with particular emphasis on soil series and soil mapping. They showed that S^2 and CV increased with the size of the area sampled. They reported, in addition, that up to one-half of the S^2 in a whole field may be present within any square meter area of the field.

The foregoing discussion illustrates the historical usage of classical statistics in describing field variability. Unfortunately, statistical tools commonly applied have severe limitations for some purposes. First, use of the SD assumes that the samples represent a random population. In the field, this is rarely, if ever, true because soil variability is patterned, as stated above (LeClerc et al., 1962). Second, the statistical mean should be accompanied by information on the range of values, low to high, and also the *location* in the field of the low and high values of the soil property in question.

A systematic, i.e., nonrandom, sample is required to determine the field locations and distributions of low and high values for any soil parameter. This approach is obviously more time consuming and requires analysis of more soil samples than the simple random (composite) sample or some variation of the stratified sample. James and Dow (1972), Dow and James (1973), and Dow et al. (1973) demonstrated the utility of intensive (e.g., square grid) sampling in fields that have extensive areas of subsoil exposure. The simple composite sample, in these cases, had practically no value in managing the whole field for uniformly high crop production.

To overcome wide variations in soil fertility levels resulting either from land-forming processes or expansion of field boundaries to include areas that were previously managed differently, a sampling and statistical procedure known as Regionalized Variable Theory (RVT) has recently been evaluated as a technique for making better fertilizer recommendations. Use of RVT requires some type of intensive field sampling procedure. With this technique, it is possible to predict S^2 at any *unsampled point in that field* without further sampling. The limitation to this technique is that results are specific to the field on which RVT was used and cannot be readily extrapolated to other fields. In other words, RVT results are site specific. However, use of this technique holds promise for better estimating fertilizer needs for situations mentioned above.

Since RVT is a new technique, a brief explanation of the process is in order. Use of RVT includes two processes, semivariograms and kriging, for segregating total field variability into three or four categories, namely nugget, sill, drift, and residual or truly random S^2 . These properties are illustrated in Fig. 3-1 and 3-2. An example of the application of RVT to soils work is that of Webster and Burgess (1980) and Assmus et al. (1985). Up to this point, RVT has been used more frequently in assaying soil physical parameters (Folorunso & Rolston, 1985; Kachanoski et al., 1985; Vieira et al., 1981) but it is finding its way into soil fertility and plant nutrition studies as well (Knighton, 1983; Knighton & James, 1985; Tabor et al., 1985). Sabbe and Marx (1987) present an excellent detailed explanation on use of RVT for sampling fields for use in evaluating soil fertility needs.

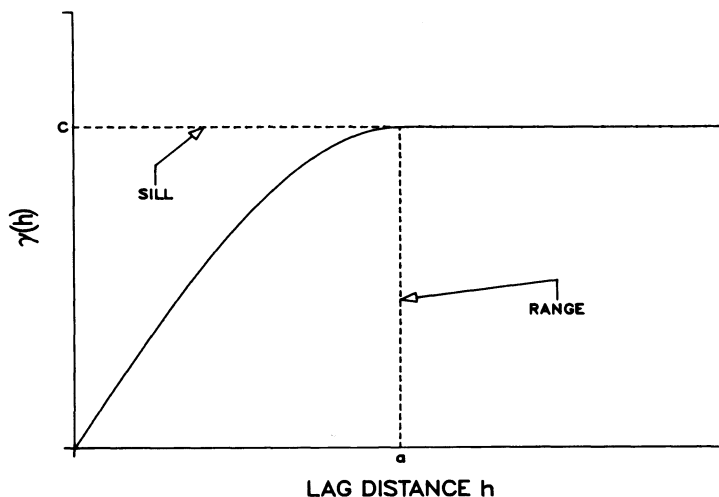


Fig. 3-1. Shape of the semi-variogram using the spherical model. Semi-variance is dependent on distance (h) between lag distance zero and a . At lag distance a and beyond semi-variance is constant, this is also referred to as the sill. Lag distance is distance between any selected reference point and any other point in the field. (Adapted from Clark, 1979.)

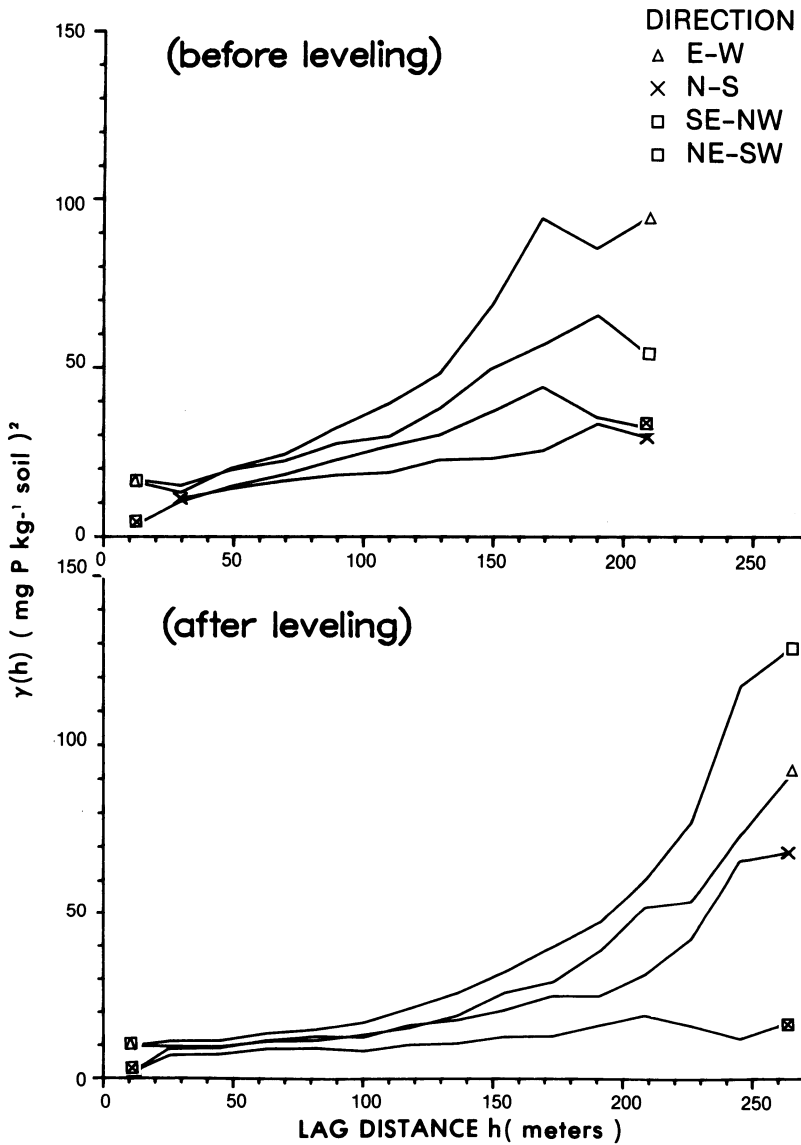


Fig. 3-2. Semi-variograms of soil test P for four directions before and after land leveling. The nugget effect is demonstrated here where the semi-variance is not zero at zero distance. Drift is demonstrated by increasing semi-variance with distance. In these examples drift varied with direction. (Adapted from Knighton & James, 1985.)

I. SOURCE AND DEGREE OF FIELD VARIABILITY

Soil variability may be classified as to vertical and horizontal direction; short, medium, or long distance; and whether the variability is natural or induced by human operations on the land.

A. Natural Variation

Soil-forming processes may cause sharply contrasting differences in the soil profile, particularly the A and B horizons. These differences relate to organic matter, pH, texture, cation-exchange capacity, and plant nutrient availability. In humid-subhumid soils, the pH usually stays the same or decreases with depth. In arid-semiarid soils, however, calcium carbonate tends to accumulate in the subsurface layers. Interbedded rock parent materials can also result in sharply contrasting differences among soils in the same field.

Ordinarily, soil samples represent the surface or plow layer, but if the subsoil is exposed by erosion, land leveling, or smoothing, sharp differences in soil properties may occur in very short horizontal distances. This may severely compound the problem of obtaining a "representative" sample of the field. An awareness that the potential exists for such variability is obviously a prerequisite to designing a proper sampling procedure.

Natural variation across somewhat longer distances is associated with slope and aspect. Soil tends to be shallower on the crest of knolls and deeper on the upland flats and lower slopes. Aspect may affect absorption and reflection of solar radiation, which in turn, affects soil temperature, water relations, and associated plant growth. Soil sampling across gradients in slope and aspect will result in an average that may mask important soil differences.

B. Human Variation

Tilling of the land and managing crops can have profound effects on field variability. The practice of land leveling, frequently done to facilitate surface irrigation in drier regions, or terracing in humid regions can result in induced variation. Tillage practices, too, will affect soil erodability and have the tendency to expose subsoils.

Different cropping systems and associated fertilizer management practices may lead to differences in organic matter amount and type as well as different residual fertilizer patterns.

Peculiar kinds of variability can be induced by fertilizer application methods. Jensen and Pesek (1962a, b) illustrated problems in crop productivity associated with non-uniform fertilizer application. It is not usually difficult to obtain uniform fertilizer distribution if the proper equipment is used. Even though fertilizer may be uniformly applied, there may be a significant degree of induced small-scale heterogeneity. The following examples illustrate these points.

Consider P fertilizer applied uniformly as a topdressing without any mixing or incorporation. The result is a large difference, depending on the rate of fertilization, between a thin P-enriched soil 2- to 3-cm layer at the surface and the soil immediately below the surface. The topdressed P may be incorporated by discing or plowing. The effect will be some redistribution with depth depending on the type of tillage involved. But tillage may or may not lead to uniform vertical distribution of fertilizer to the depth at which it is incorporated (Hurlburt & Menzel, 1953).

Another sharp contrast in soil variability may be observed when fertilizer is injected, banded, and sidedressed. This leads to high variability along lines normal to the direction of fertilizer application. This cyclic variability results in high concentrations of the fertilizer element at the point of injection, separated by somewhat uniform concentrations of the element between the lines of injection. This kind of variability will be diminished by subsequent tillage operations (e.g., plowing) that tend to stir the plow layer.

The nature of the applied fertilizer itself has an effect on soil heterogeneity. For example, nitrogen, despite the specific form applied, tends to nitrify in soil over time to nitrate, a completely soluble form. Nitrates diffuse in the soil solution with infiltrating water, leading to more soil homogeneity in comparisons with the high heterogeneity induced at the time of fertilizer application. It is apparent that soil nitrate may vary greatly over time at different points in the soil profile following fertilizer applications.

Other fertilizer elements contrast sharply with N in terms of soil mobility. For example, potassium reacts readily with the exchange complex and, except in soils with very low cation exchange capacity, will essentially be immobilized. Phosphorus fertilizer reacts rapidly upon soil application with other chemical constituents (e.g., Ca, Al, and Fe) to form fairly insoluble and, therefore, immobile compounds. Generally, researchers agree that P will diffuse in the soil away from the fertilizer pellet and enrich a soil volume no more than about two or three diameters of the original pellet. The result is very high heterogeneity on a microscale. Again, tillage operations completed after P fertilizer equilibration will mix the P-enriched soil.

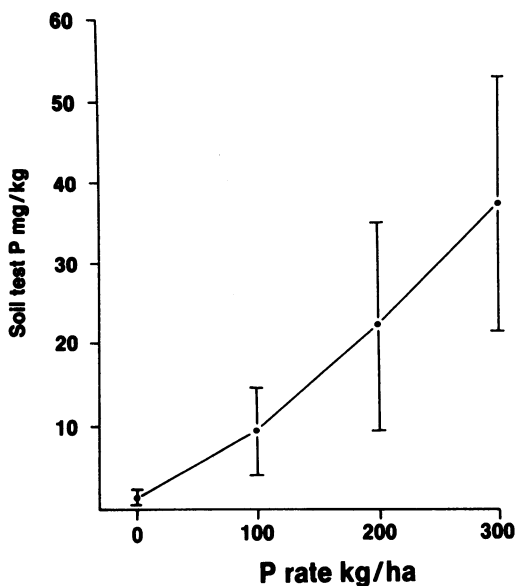


Fig. 3-3. Micro-variation: variability of soil test P in 30 soil cores of 2.5-cm diam. as related to P fertilizer rate. The fertilizer was applied broadcast-plowdown in spring and the soil was sampled in autumn. Vertical line segments represent the 95% confidence limits. (Adapted from James & Dow, 1972.)

C. Point-to-Point Variability

Soil differences between points on the landscape present the basic challenge in designing an effective soil-sampling procedure. Soil variability is classified into three distance categories—micro-, meso-, and macro-variability to describe appropriate soil-sampling technique.

Micro-variation refers to soil variation between points separated from 0 to 0.05 m. Figure 3-3 illustrates this type of variability. The data of Fig. 3-3 were obtained by analyzing individual soil cores, that were about 2.5 cm in diameter and 25-cm deep, for available P (NaHCO_3 method). Figure 3-3 shows that the average effect of fertilization was a smooth curvilinear increase in soil test P (STP). But STP varied widely (i.e., micro-variation) among soil cores on all plots except the ones receiving no fertilizer.

Meso-variation is soil variation between points separated by 0.05 to 2 m. This kind of variability is demonstrated in Fig. 3-4 which shows that distribution of STP along a 1.78-m sampling transect that covered two potato rows (*Solanum tuberosum* L.) rows. Extreme soil variability on the mesoscale may be induced by fertilizer placement.

Macro-variation is soil variation between points separated by distance > 2 m. Macro-variation is associated with natural soil processes, but human's soil management practices also can have a significant influence on this type of variation. Figure 3-5 illustrates management-induced macro-variability. The mean whole-field STP was 8.40 mg kg^{-1} with $\text{SD} = 4.84$. A moderate rate of fertilizer P would be recommended for this level of STP. However, 19.2% of the field was very high in available P and would yield no immediate benefit to a fertilizer application. On the other hand, 34.8% of the field was low in STP needing a moderately high rate of fertilizer P. In addition, 18.4% of the field was very low in P and needed a high rate of fertilizer

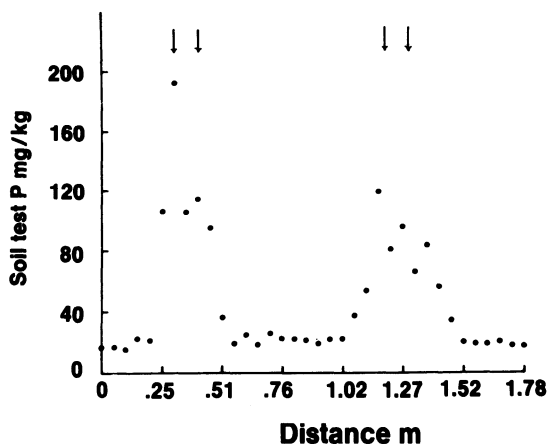


Fig. 3-4. Meso-variation: scatter diagram of soil test P in individual cores (2.5-cm diam.) collected on a transect that spanned two potato rows. Arrows indicate approximate positions of sidedressed P fertilizer at planting time. Soil samples were collected in autumn after harvest. Dispersion of soil test P values was related to local mixing by the digging equipment at harvest time. (Adapted from James & Dow, 1972.)

to completely eliminate soil fertility as a limiting factor to crop growth. In other words, if the field mean STP was the only criterion for fertilization, only 27.6% of the whole field would receive the appropriate amount of fertilizer. Thus, sampling methodology clearly has significant practical implications, especially where the field is very heterogeneous.

Another problem associated with low-P soil in Fig. 3-5 is the soil-texture differential between surface and subsoil. The surface soil at this site is clas-

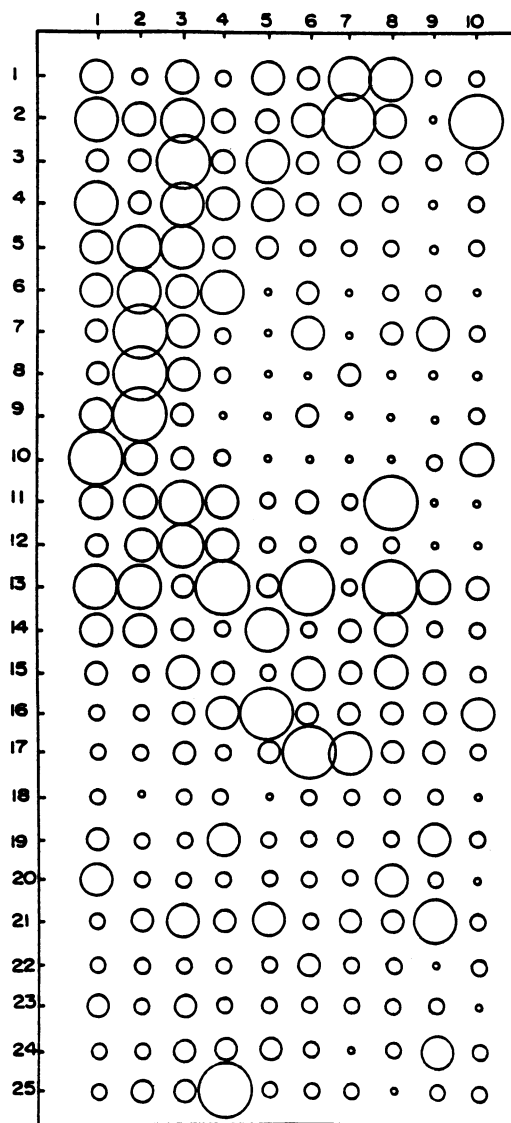


Fig. 3-5. Macro-variation: soil test P variability determined from point soil samples collected on a 15.2-m square grid after land leveling. Sampling column and row numbers are indicated on margins. For data shown, no. of samples = 230, \bar{X} = 12.6 mg of P kg⁻¹, SD = 62.43, range = 2 to 46. The circles, small to large, represent the STP categories <5, 6 to 10, 11 to 15, 16 to 20, and >20 mg of P kg⁻¹. (D.W. James, 1983, unpublished data.)

sified as silty clay loam. The subsoil is clay. Because of the variable texture in the smoothed field, surface irrigation water infiltration rate and soil water-holding capacity would be as variable as the STP. Limitations in P availability may be overcome through judicious applications of fertilizer. However, no practical treatment is known that will decrease the spatial variability of soil water intake rate and holding capacity, at least in the short term.

II. SAMPLING METHODS

Soil-sampling procedure should be adapted to the degree of variability on all scales, micro-, meso- and macro. In this sense, it is apparent that some fore-knowledge of field conditions is required to determine what is appropriate. This fore-knowledge would include such things as exposure of subsoil from land leveling or erosion; kind and amount of fertilizer applied in previous seasons, and whether the fertilizer was applied broadcast, sidedress, band; and the degree of soil mixing that may have occurred subsequent to fertilization by plowing, disking, tillage to control weeds, and rowhilling. Sampling techniques are broadly defined in the following discussion of uniform and non-uniform field conditions.

A. Uniform Fields

Uniform fields signify field areas that are similar in regard to slope, aspect, management history, cropping and fertilization, and if possible, crop appearance during the growing season. *Uniform* requires that macro- and meso-variations be nonsignificant. Sampling procedures that fully satisfy these conditions involve the collection of randomly selected soil cores that are mixed together into one sample. This is the customary random composite soil sample.

To be truly random, the soil cores should be taken from field segments within the uniform area that are randomly selected. It is usually not practical, however, to divide a field area into segments and, after numbering them, sample a randomly selected set of segments. In practice, it is common to collect soil cores by following a zigzag path where a conscious effort is made to force the path into corners and along edges as well as the central parts of the area being sampled.

Thus, realistically, "random composite soil samples" are subject to judgment in terms of both field segregation into uniform areas and the path followed to collect the sample. When the field history is well known, this type of sampling scheme can be completely adequate in terms of developing an appropriate fertilizer management program.

Micro-variation will be adequately controlled if the number of soil cores collected is sufficient, e.g., 25 to 30 cores per sample and if the composited cores are thoroughly crushed and mixed.

B. Non-uniform Fields

Nonrandom sampling: Where macro-variation is large, a nonrandom soil sampling procedure is recommended. A major objective in nonrandom sampling is to understand not only the average field condition but also the extreme high and low values, and what is more important, the specific locations of the field extremes. By its nature, nonrandom soil sampling requires numerous point soil samples. To do this, a field grid is developed by placing marks at regular intervals in two directions and collecting soil samples at the grid line intersections. Spacing between grids will vary with the degree of detail needed to satisfy the sampling objectives. Typical grid spacings will lie between 15 and 30 m. Within this range, the number of samples per hectare would lie between 45 and 12 depending on where the beginning grid point is with respect to field boundaries.

A point soil sample is collected from each grid point. This consists of 8 to 10 cores from a circle of about 1-m diam. centered over the point. The number of soil cores should provide a total soil volume of practical size to perform the needed chemical or physical analyses. Eight to 10 cores are usually sufficient to overcome micro-variation.

Each point sample is analyzed and the results are plotted on a field map in relation to their grid location. Soil test isolines (contours) are then drawn which stratify the field into selected soil test ranges. After establishing the field location of soil test categories, fertilizer rates can be adjusted for each field stratum. As an example, soil test P strata can be visualized in the field represented by Fig. 3-5. If, in this example, rates of P fertilizer are applied appropriate to the STP conditions, then the STP will become more homogeneous and the intensive grid-sampling procedure would not need to be repeated in subsequent years.

Random sampling: High meso-variation, the type of soil variability peculiar to injection or band-applied fertilizer, has always been a special challenge in regard to obtaining representative soil samples. With minimum tillage and no-tillage practices becoming more widespread meso-variation must be studied more intently if soil sampling is to be adequate for diagnostic soil testing.

Band-applied fertilizer generates two interlacing populations consisting of (i) the bulk soil not affected by fertilization, and (ii) compact bands spaced at regular intervals that are highly enriched by fertilization. The bulk soil would be characterized by one set of \bar{X} and SD values and the enriched band soil would be characterized by another set of \bar{X} and SD values. As a practical matter, these two populations need to be treated as one so as to obtain an adjusted average soil fertility test value that truly reflects the overall conditions encountered by plant roots.

Soil sampling of a field with significant meso-variation requires many soil cores to obtain the proper averaging of the two soil populations. The soil sample is analogous to the above-described random composite sample except that a much greater number of soil cores are needed. In addition, the

primary sample would be much larger, requiring special handling to thoroughly crush and mix the collected soil cores followed by sample reduction through a multiple splitting process.

The specific number of soil cores needed to satisfy the conditions of significant meso-variation requires further investigation but it is evident that it will depend on the following parameters:

1. Distance between fertilizer bands.
2. Width of the fertilizer band.
3. Diameter of the sample coring tube.
4. \bar{X} and SD within the band.
5. \bar{X} and SD of the bulk soil between bands.

It is apparent that the number of individual soil cores in the intensive composite sample will need to be four- to fivefold larger than the number needed for the customary random composite sample.

III. DEPTH OF SAMPLING

Soil-sampling depth is most often the plow layer, e.g., 0 to 17 cm (0–6 $\frac{2}{3}$ in.) or 0 to 20 cm (0–8 in.). Traditionally, the plow layer is generally estimated to weigh 357 Mg ha⁻¹ (2 000 000 lb/acre). Many studies have been reported in the literature that show incorporation of lime and the immobile fertilizer nutrients to plow depth on acid and infertile soils to be effective in increasing crop yields as compared to not liming or fertilizing. In a review of research reported on depth of lime incorporation, Wells (1980) concluded that, with few exceptions, nearly all yield increase because of liming was obtained by incorporation within the plow layer. Deeper incorporation of lime rarely improved yields. As pointed out by Shoemaker (1964), this depth (volume) factor needs to be considered when sampling shallower or deeper than the plow layer to adjust rates of lime and fertilizer to the proper soil volume basis. The concern about adjustment of recommended rates on a soil volume basis is because of widespread use of tillage implements which till deeper than 17 to 20 cm. There is as much or more concern about proper manipulation of rates and volume with advent in recent years of the various conservation tillage practices that do not mix lime and fertilizer throughout the traditional plow layer.

A. Conventional Tillage

In conventional tillage, soil is somewhat mixed to the depth to which the primary tillage implement penetrates and additionally mixed in the surface 7 to 10 cm (3–4 in.) by secondary tillage as with a disk harrow. By this process, lime and the immobile fertilizer nutrients become somewhat uniformly mixed throughout the plow layer over a few years. Figures 3–6 and 3–7, made from data reported by Randall (1980), show the effect of the tillage method on long-term soil test values for P and K. As shown, concentra-

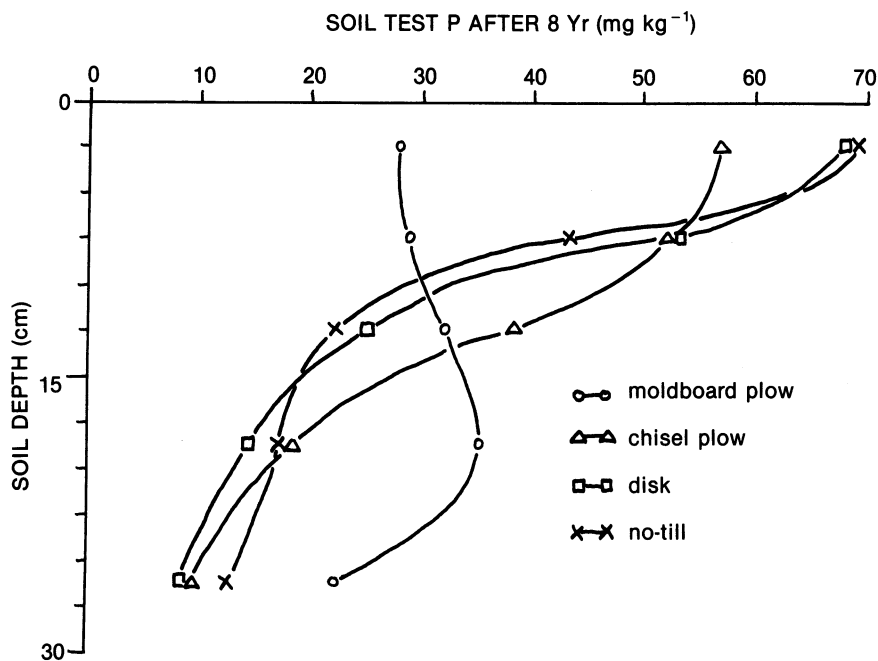


Fig. 3-6. Effect of tillage system on distribution of soil test P levels. (Adapted from Randall, 1980.)

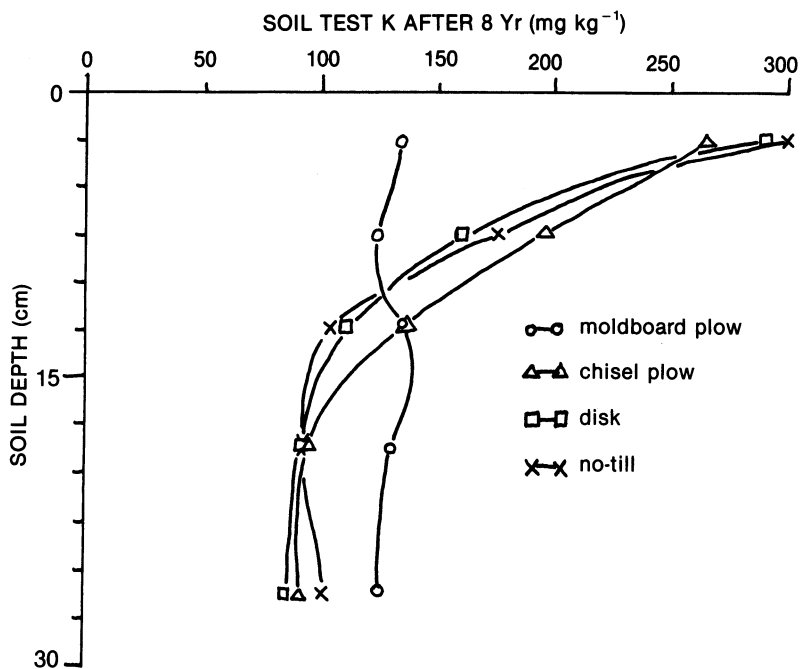


Fig. 3-7. Effect of tillage system on distribution of soil test K levels. (Adapted from Randall, 1980.)

tion of available P and K is much more uniform throughout the plow layer with conventional plow-disk tillage as compared to the conservation tillage methods of chisel plow-disk, disk only, or no till. For routine sampling of conventionally tilled soils, the plow layer sample depth is considered satisfactory for determining level of soil acidity and immobile nutrients.

In the semiarid and some humid areas, however, where sampling for N content is recommended, deeper samples are necessary. As Meisinger (1984) summarized, recommended depths for soil nitrate sampling range from 30 to 180 cm (12–72 in.), but most often from 60 to 120 cm (24–48 in.). These depths correspond to those suggested by Nelson et al. (1967), James (1971, 1978), and James et al. (1977) for nitrate testing in irrigated soils. Variation in depth recommended for deep sampling for nitrates was because of site-specific factors such as type of crop, type of soil, and prevalent soil conditions.

B. Conservation Tillage

Concern over soil and water conservation has resulted in development of several systems which involve much less mechanical tillage than the traditional plow-disk systems. This results in mixing of a much smaller volume of soil and a concentration of lime and immobile nutrients at shallower depths than from conventional tillage systems. Although there are several conservation tillage systems being used, chisel plowing followed by spring disking, disking only, and no-till are the most common. Ridge-till is becoming important in some areas. The effect which continuous use of these systems has on depth to which P and K are incorporated is shown in Fig. 3-6 and 3-7. These results are similar to other published reports about influence of conservation tillage on depth to which lime and immobile nutrients are incorporated. Both disk only and no-till result in a highly concentrated layer of soil test extractable P and K in the surface 0 to 7.5 cm (0–3 in.) with much lower concentrations below 7.5 cm (3 in.) as compared to conventional moldboard plow tillage. Chisel plowing incorporates P and K a little deeper than no-till or disking, but not as deep as moldboard plowing.

This raises the question of how to sample conservation tillage fields to best determine lime and fertilizer needs. Whitney (1982) reported on a survey from several states, that most had modified their recommended sampling depth for conservation tillage to shallower depths than the traditional plow layer depth. He suggested sampling such fields to a depth of 5 to 10 cm (2–4 in.). Such shallow sampling, particularly for no-till planted crops is currently recognized as more effectively evaluating soil fertility status than deeper sampling. Wells (1985) has reported good corn (*Zea mays* L.) yields from surface application of P and K on low testing no-till fields even though test levels below 7.5 cm (3 in.) remain low. Mengel (1982) showed increased root distribution in the surface layer of no-till corn fields which presumably accounts for this.

In addition, this shallower sampling procedure more effectively defines surface acidity levels that have been shown by Kells et al. (1980) to influence activity of some herbicides, particularly the s-triazines. Deeper sampling di-

lutes the extremely acid conditions that develop in the soil immediately below the surface mulch residues which accumulate in continuous no-till systems. In some cases, even shallower sampling at the 0 to 5 cm (0–2 in.) depth is used to more effectively describe the surface acidity of no-till fields. Mengel (1982) recommended two sampling procedures for conservation tillage corn: (i) sample the 0 to 10 cm (0–4 in.) and the 10 to 20 cm (4–8 in.) depths for all reduced tillage fields and on all no-till fields where N is injected below the soil surface, and (ii) sample no-till fields where N is surface applied at the 0 to 5 cm (0–2 in.) and 5 to 20 cm (2–8 in.) depths.

Another conservation tillage technique, ridge-till, is a rapidly growing practice in some areas and presents a unique problem in soil sampling. As described by Randall (1982), surface-applied nutrients are swept from row middles onto the ridge during the ridging process, enriching the ridge fertility at the expense of the row middles. This management practice leads to a type of meso-variability, and intensive sampling would be needed to obtain a representative sample. Moncrief et al. (1984) recommend a 0 to 15 cm (0–6 in.) sampling depth for ridge-till. They recommend sampling after planting but before ridging to lower variability. If sampling cannot be done before ridging, they suggest taking samples half way up the ridge.

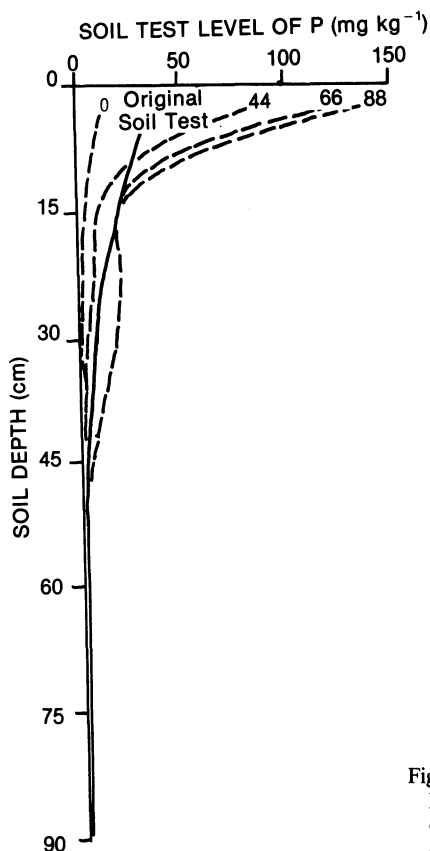


Fig. 3–8. Soil test P levels in an alfalfa sod following 6 yr annual topdressing of P at 44, 66, and 88 kg ha⁻¹. (Adapted from Vaught et al., 1977.)

Currently, the prevailing thought in sampling conservation tilled fields is to sample at a shallower depth than for conventional tillage to monitor surface acidity and buildup of immobile nutrients. Concurrent sampling below the shallow sample to a depth of 15 to 20 cm (6–8 in.) enables monitoring of nutrient movement deeper into the soil and the degree of stratification.

C. Permanent Sod

Vast acreages of sodland exist throughout the USA that are fertilized and managed for hay or pasture production. Typically, sampling of the traditional plow layer has been recommended when fields are conventionally plowed to establish the various sod-forming crops. Lime and fertilizer are often recommended for topdress application onto sods between intervals of establishment or re-establishment. Annual topdressings of sodland, as with conservation tillage, result in a buildup of immobile nutrients in the surface 0 to 5 cm (0–2 in.). Wells and Parks (1961) and Vaught et al. (1977) showed that annual topdressings of P and K to alfalfa on silt loam surface-textured soils resulted in little movement of P and K below 7.5 cm (3 in.) even at high annual rates over several years. Figures 3–8 and 3–9 from Vaught et al. (1977)

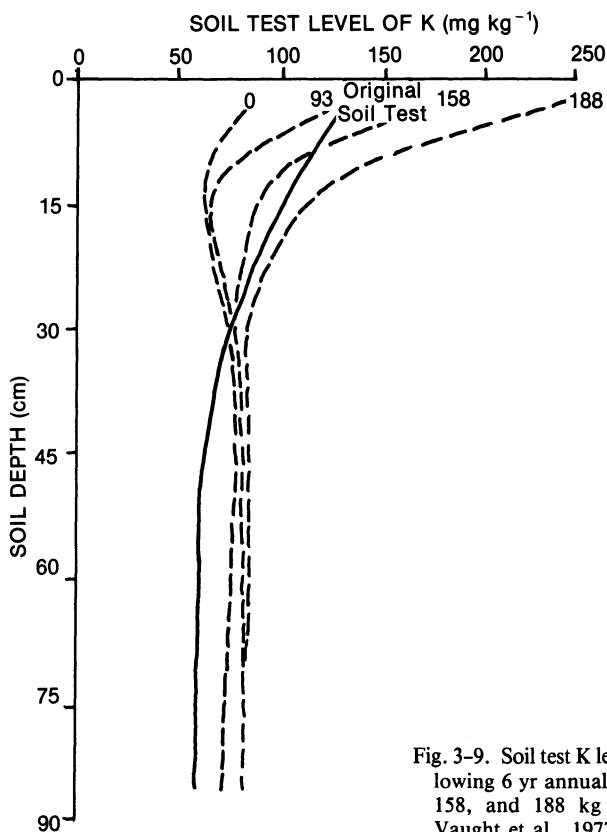


Fig. 3–9. Soil test K levels in an alfalfa sod following 6 yr annual topdressing of K at 93, 158, and 188 kg ha⁻¹. (Adapted from Vaught et al., 1977.)

illustrate soil-profile distribution of soil test P and K levels after 6 yr of annual topdressings. High yields of 13.4 t alfalfa dry wt. ha⁻¹ (6 ton/acre) were maintained at the lowest level of fertilizer P and K applied annually.

With the advent of no-till drills for seeding forage crops in recent years and with shallow tillage to 7.5 to 10 cm (3–4 in.) often used to renovate pastures, many sod fields rarely have lime and fertilizer mixed into the traditional plow layer by primary tillage tools. Consequently, Thom et al. (1982) in Kentucky recommend sampling of such fields only to the 10 cm (4 in.) depth.

IV. EFFECT OF TIME OF YEAR ON SAMPLE COLLECTION

As discussed by Peck and Melstead (1973), seasonal variation in soil test values should be expected because of variations in factors that influence mineral accumulation by plants and recharge of the soil solution content of minerals as plants remove them from solution. They point out that it is difficult to quantify how much this can change soil test values at different times of the year. Their review of published literature indicated that soil acidity increased in acid soils during the growing season (May–September) but did not consistently vary in alkaline soils. Data from tobacco experiments in Kentucky by Reneau et al. (1968) on an acid soil showed similar results. Soil samples of the 0 to 15 cm (0–6 in.) depth of non-irrigated unfertilized soil taken at weekly intervals from April through August showed that pH values dropped from an initial value of 6.0 in April to 5.3 by mid-May and varied between 5.3 and 5.6 throughout the remainder of the summer. When fertilizer was applied, the resultant salt effect dropped pH to 5.1 to 5.2 by mid-June where it remained throughout July and August. On soil that was irrigated, pH dropped to the 4.8 to 5.2 range. Additional studies on tobacco by Sims and Atkinson (1974) showed similar results, with soil pH dropping 0.2 to 0.6 units during the summer, the magnitude of drop being influenced by fertilization. It would seem reasonable to expect a seasonal drop in pH values from spring to autumn because of the soluble salt effect resulting from mineralization of organic residues, weathering of minerals, or application of soluble fertilizers. In areas where there is enough rainfall during the winter to leach soluble salts deeper into the soil, pH values would generally be expected to return to near the level from which they dropped.

Although there is little published data on seasonal effect on soil test readings for P and K, the general consensus is that they would likely decline somewhat from spring to autumn. Childs and Jencks (1967) reported from studies on three soils in West Virginia that P and K soil test values declined progressively from annual high values in November to December to annual low values in July. The differences in readings were great enough to influence the amount of P and K fertilizer recommendations for crop production. Lime requirement and pH tests in their study showed the same seasonal effect as previously described.

In general, soil samples taken in late summer or early fall will probably test lower in pH and plant-available P and K than if taken any other time of year. Highest readings would likely be measured on samples taken during the winter or early spring months. Recommended rates of lime and fertilizer based on late summer or early fall samples would likely be higher than those based on winter or early spring samples. Particularly for medium or lower testing soils in P and K and on very acid soils, the late summer or early fall samples may more accurately reflect the need for lime, P, and K than samples taken during the winter or early spring.

V. SOIL SAMPLING TOOLS

A wide array of sampling equipment is available which will perform well in pulling soil samples, ranging from hand tools to vehicle-mounted hydraulic driven power probes or augers. The main consideration in selecting a tool for sampling is that it can easily be cleaned between composite samples taken in a field and that it accurately samples the intended depth. Hand probes (tubes) are probably the most widely used tool. Preferably, they should be of stainless steel construction to minimize oxide contamination of samples, which is particularly important in sampling for micronutrients such as Fe and Zn. Auger-type sampling tools (screw or bucket augers) are more effective than probes or tubes in sampling gravelly or rocky soils.

The container into which composite soil samples are placed is an extremely important component of sampling. A clean, plastic bucket is probably the best container to use since it is light weight, easily cleaned, will not contaminate the sample with oxides, and can easily be used to mix up the composite samples taken in each field. Peck and Melsted (1973) described good sampling equipment as that which should:

1. Take a small enough equal volume of soil from each subsampling site so that the composite sample will be of an appropriate size to process for analysis.
2. Be easy to clean.
3. Be adaptable to dry sandy soil as well as moist sticky soil.
4. Be rust resistant and durably constructed to resist bending or breakage.
5. Be relatively easy to use and thus provide for fairly rigid sampling of a field.

As they point out, the most important feature of a sampling tool is that it will provide uniform cores or slices of equal volume at all spots within the composite sampling area.

VI. HANDLING SAMPLES

A. Prevention of Contamination

Great care should be taken to prevent sample contamination during the process of collection and sampling handling. Common sources of contami-

nation are dirty sampling tools, dirty containers, cigarette or pipe ashes, drying samples on dirty paper or in dusty places. Galvanized metal containers should never be used for samples to be tested for Zn. Empty coffee cans can be a major source of Zn contamination. Likewise, samples to be tested for B should not be placed in or on Kraft paper bags since such paper can be a B contaminant. The best preventative for contamination is use of clean tools, clean plastic buckets, clean plastic bags, and use of containers supplied by testing laboratories for packaging the sample to be sent to the lab.

B. Mixing

The subsamples or cores of soil taken from a field should be thoroughly mixed. Probably the most difficult subsamples to mix are those which were taken either too wet or too dry for crumbling by hand. Samples too dry to break apart by hand must be crushed in some manner before the subsamples can be mixed well, while samples taken too wet must be dried to the point they can either be hand or mechanically crushed. If soil is at the proper moisture content to permit hand crushing, the final mixing of the subsamples can be made easier by crushing each sample as it is taken from the sampling tool and placed into the carrying container. The basic principle to keep in mind is that in reducing the volume of subsamples taken from 1 to 4 L (approx. 1–4 qt) to about one-half liter (approximately 1 pint) for packaging and sending to the laboratory, the amount packaged must represent an average composition of all the subsamples taken. Unless the subsamples are uniformly crushed to a fairly small particle size (2–5 mm) (1/8 to 1/4 in.), it will be difficult to thoroughly mix the subsamples into one homogeneous composite sample.

C. Drying Samples

If samples taken from a field are too wet to crush for mixing, they should be dried sufficiently for crushing to a friable, uniform particle size to prepare the composite sample. It is not necessary to take the sample to complete dryness for this purpose. Wet samples should be dried at temperatures no greater than 35 to 50 °C (approximately 100–120 °F). Higher drying temperatures can alter the nutrient solubility of the organic and mineral fractions of the soil. Great care should be taken to prevent contamination during the drying process.

D. Splitting the Composite for Laboratory Analysis

As previously mentioned, the composite sample taken from a field will be too large for sending to the soil testing lab, and must be split into a smaller volume. This requires that the composite sample be uniformly mixed prior to splitting. One unbiased technique to use for sample splitting would be to split the mixed composite into halves, split one of the halves in half and if still too large for the sample container, split the sample in half again to ob-

tain a subsample of the whole composite for sending to the laboratory. Several variations of such a splitting technique are possible.

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Chapter 4

Soil Test Correlation, Calibration, and Recommendation¹

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The basic aim of soil testing is to assess nutrient status, thereby identifying current and potential need for fertilization, monitor the effects of cropping practices on soil fertility, and assist in developing fertilizer recommendations.

There is no doubt about the existence of a relationship between soil nutrient status and crop growth. The relationship, however, is often obscured by the influence of many other growth factors. Knowledge of the soil's ability to supply nutrients, the amount of nutrients required for crop growth, and the influence applied nutrients have on crop growth is all needed to improve fertilizer recommendations. It must be understood, however, that the influence of fertilizer on crop growth during the growing season will largely depend on weather conditions during the growing season and on crop management intensity. Variable response to applied nutrients from unpredictable growing season conditions is probably the main reason why so many processes, systems, and models have been proposed to convert basic soil-fertility data into soil-testing programs.

In addition to using soil tests to help identify crop production constraints such as nutrient deficiencies, they also are used to identify toxic levels of particular nutrients and other elements or of soluble salts in general. Also, they are used to determine soil pH, lime requirement, and organic matter.

In this chapter, soil test development will be divided into the following steps: (i) correlation, (ii) calibration, and (iii) interpretation of data to develop recommendations. These terms are not clearly defined in the literature and are sometimes used interchangeably.

In this text, *correlation* is defined as the process used to determine if a soil nutrient, as extracted by a soil test, and crop response to added nutrient are so related that one directly implies the other. In other words, correlation

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is the process of selecting the best soil test for the soils of the area. Soil test *calibration* is the process of ascertaining the degree of limitation to crop growth or the probability of getting a growth response to applied nutrient at any soil test level. The amount of extractable nutrient is usually expressed as low, medium, high, or as a range of critical concentration. The final step is to develop fertilizer *recommendations*. This step is often spoken of as soil test interpretation. Individual interpretation and experience are evident in this step and are the cause of much controversy and confusion in soil testing. Examples will be given demonstrating several ways to interpret the same data.

In spite of these problems, site specific estimates of nutrient status, as provided by soil tests, can be the most efficient method for the rational use of fertilizers in producing crops.

I. SOIL TEST CORRELATION

Soil test correlation is the process of determining whether there is a relationship between plant uptake of a nutrient or yield and the amount of nutrient extracted by a particular soil test (Corey, 1987). This relationship can be determined either mathematically or graphically.

Correlation research is usually conducted in two steps: an exploratory fertilization trial in the greenhouse with many soils followed by trials with fewer, carefully selected soils in the field. The advantage of growth chamber studies is better control of environmental factors and soil homogeneity. Greenhouse results, however, may not be directly transferable to field conditions (Corey, 1987).

A. Soil Extraction

Most soil tests involve the extraction of nutrient from a soil sample. One of the first soil tests was that of Daubeney (1845). It involved extracting the soil with carbonated water. This test was never put to practical use because of analytical difficulties. Many other extracting solutions have been suggested and used to extract nutrients from soil samples. The reason some extractants fail today is not because of analytical problems but because the amount of nutrient extracted does not correlate with either plant nutrient uptake or yield.

In addition to the extractant itself, the other important aspect of a soil test is how the soil is extracted. Some of the important factors of a soil test procedure, such as soil/solution ratio, extraction time, shaking speed, shape of extraction flask, are discussed by Grava (1980) and Munter (1988). A soil test not only refers to the type of solution used in extracting a nutrient but also how the extraction is accomplished.

The following sections discuss methods used to correlate the amount of nutrient extracted from the soil with plant nutrient uptake or yield of greenhouse and field trials.

B. Greenhouse Trials

Greenhouse trials are an excellent tool to determine the relationship between nutrient availability as measured by soil test and nutrient uptake by plants. Greenhouse trials are better than field trials for this purpose because the influence of uncontrolled variables such as subsoil, climate, and soil variability can largely be eliminated. It is important that many soils be used to increase confidence that the results will be accurate and not because of chance. It is also important to select soils with a wide range in nutrient availability and that the nutrient range approaches a normal distribution. This is especially true if results are analyzed mathematically because the usual method of calculating correlation coefficients assumes a normal distribution of the variables (Snedecor & Cochran, 1971).

In the case of nutrients such as nitrate-N and chlorine that can readily move in the soil or are mineralized from organic matter, field correlation studies are necessary.

1. Mathematical Correlation

Correlation coefficients for various soil tests can be compared directly. A correlation coefficient of $r = 1.0$ indicates a perfect correlation and a coefficient of zero indicates no relationship. In addition to the determination of correlation coefficients, a regression analysis is often done to mathematically express the change in nutrient uptake as soil test changes (Corey, 1987). This enables one to compare the relationship between nutrient uptake and soil test. When there are numerous variables that may influence nutrient uptake or yield, various multiple regression techniques have been used in an attempt to determine the relationship. These techniques are often used to consider interactions.

2. Cate-Nelson Method of Soil Test Correlation

In contrast to mathematically determining correlation, the simple graphic method of Cate-Nelson (Cate & Nelson, 1965) has practical advantages in addition to showing whether good correlation exists, it splits the data into two populations (soil test calibration). Thus, it acknowledges the basic capability of soil tests, which is to separate soils that are likely to respond to added nutrient from those that are unlikely to respond. In addition, outlying data points can be identified readily in a scatter diagram and isolated for further study. When used to analyze greenhouse yield data, it can give a rough approximation of the critical soil test level, which will be of aid in selecting field sites.

The Cate-Nelson Method plots percentage yield against soil test (Fig. 4-1) to give a visual indication of the reliability of the soil test. If the majority of points on the graph have a low percentage yield when the soil test is low and a high percentage yield when the soil test is high, the soil test being studied accurately predicts the need or lack of need for a nutrient. In other words, the soil test level is well correlated with response to added nutrients. Many

points in the negative quadrants (Fig. 4-3) indicate the soil test is not well suited to the soils of the area or that there is no correlation between soil test values and plant response to the added nutrient. Steps in the Cate-Nelson Graphical Method are:

1. Determine percentage yield values for each fertilizer rate trial.

$$\text{Percentage yield} = \frac{\text{Yield at zero level of nutrient studied}}{\text{Yield when all nutrients are adequate}} \times 100$$

2. Determine soil test values for nutrient being studied.
3. Plot percentage yield (Y-axis) vs. soil test value (X-axis) on arithmetic graph paper (Fig. 4-1).
4. Draw two intersecting perpendicular lines on a clear piece of plastic. Label the top right and bottom left quadrant with a + and the bottom right and top left with a - (Fig. 4-2).
5. Place the overlay over the graph moving it horizontally or vertically until the maximum number of points are in the two positive quadrants (Fig. 4-3).
6. If nearly all of the points are in the positive quadrants, the test is accurately predicting response. Soils with a low soil test should have a low percentage yield (large response to added nutrient) and soils with a high soil test should have a high percentage yield (little or no response to added nutrient). If many of the points cannot be placed in the positive quadrants, look for another test or try to discover why these soils are outliers. The horizontal line in Fig. 4-3 will usually fall between a percentage yield of 80 to 90. Percentage yields above this range are usually not statistically significant increases in yield. Occasionally, percentage yields of more than 100 are obtained.

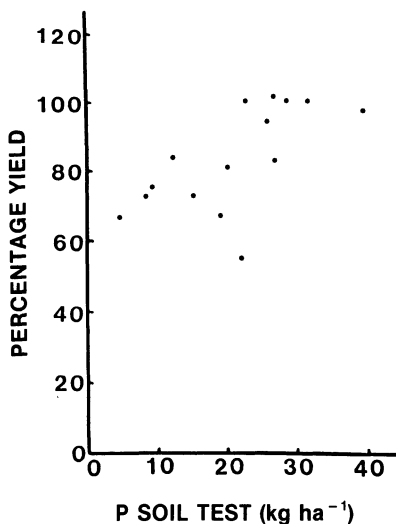


Fig. 4-1. Scatter diagram of percentage yield of wheat vs. soil test P by the Olsen method (data in Table 4-1).

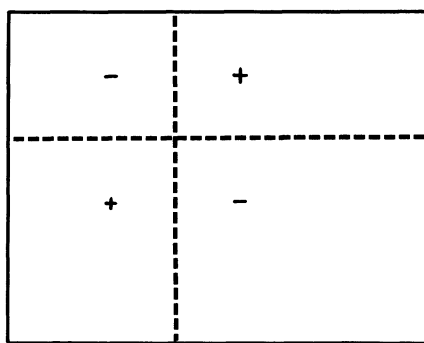


Fig. 4-2. Format for clear plastic overlay used in the Cate-Nelson graphical method of soil test correlation.

In addition to simplicity (Waugh et al., 1973; Ayodele & Agboola, 1985), this method:

1. Indicates whether or not there is a good correlation between soil test and yield response. If nearly all of the points fall in the positive quadrants, there is a good correlation. If points are equally distributed in all quadrants, the correlation is poor.

2. Indicates the soil test critical level, the point above which response to added nutrient is unlikely (Fig. 4-3).

3. Gives results that are not biased by a few outliers. Outliers can be identified readily for further study. Outliers may be caused by complete unavailability of added nutrients, a high level of the nutrient in the subsoil in the case of field trials, or some points may be in the upper left quadrant because another factor was more limiting. It must be remembered that the purpose of greenhouse trials is only to determine if there is a relationship between a soil test and response to added nutrients. Field trials must be conducted to determine how well the test performs in the field and to obtain final calibration and interpretation data.

C. Field Trials

Preliminary greenhouse data are useful to compare different extraction methods but field trials are necessary for final selection. Plant growth and yield are functions of many variables that can be grouped into soil, crop, climate, and management categories (Fitts, 1955). Poorer correlations are obtained with field trials because the uncontrolled variables are less uniform in the field than in the greenhouse. Correlations using field data can be improved, however, by plotting relative yield rather than absolute yield, yield

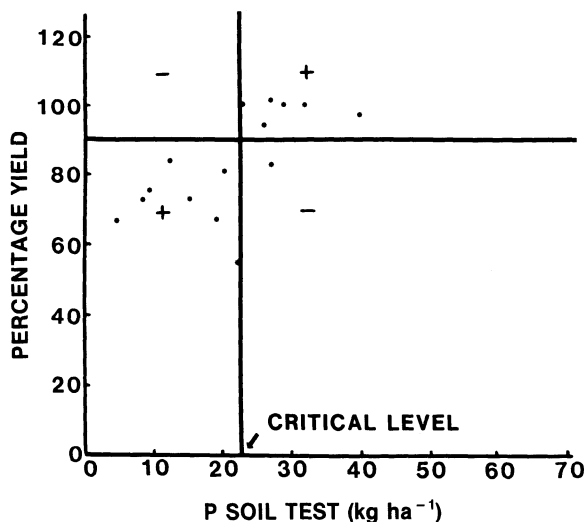


Fig. 4-3. Scatter diagram of percentage yield vs. soil test showing the soil test critical level determined by the Cate-Nelson procedure.

response, or nutrient uptake as a function of soil test values. Relative yield, also known as percentage yield, is the yield of the treatment with adequate but not excessive amounts of all nutrients other than the one being correlated, divided by the maximum yield from the nutrient studied with optimum amounts of other nutrients times 100. The reason relative yield results in a better correlation is that the influence of some of the uncontrolled variables is eliminated (Bartholomew, 1972). Relative yield cannot be used to determine economic rates of nutrient application because it does not take into consideration absolute yield level.

Field trials should be multiple rate so that the information obtained can be used not only for correlation and calibration but also for developing recommendations from the soil test that is finally selected. As with the greenhouse study, field sites chosen should range from low to high in the nutrient under investigation. Because most soils are inherently variable, a separate soil sample should be taken from each plot if at all possible. It will help explain yield variability within a site.

Use five or more rates of the nutrient being studied. The lowest rate should be zero and the highest rate should be more than enough to obtain maximum yield. It is important that the interval between rates be relatively small and well spaced within the response range to determine the point or area where no further response occurs. The number and size of plots per site should be selected to minimize effects of soil variability and yet be practical.

More reliable information can be obtained by controlling interactions when it is possible. Although emphasis has been placed on nutrient interactions, they are of little importance when other growth influencing factors are maintained at favorable levels. Much of the interaction occurs when comparing the O rate of a single nutrient with adequate rates of another nutrient (Anderson & Nelson, 1975).

All treatments should be replicated three or more times, depending on the crop. High plant population crops such as wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) require fewer replicates than low plant population crops such as potato (*Solanum tuberosum* L.). In production areas where crop response varies widely with year and location, it is of greater value to have more sites and fewer replicates than a lot of replicates and few sites. A more complete discussion of the establishment of field trials is given by Hunter and Fitts (1969).

Field data as well as greenhouse data can be analyzed by plotting relative yield vs. soil test to determine how well each soil extractant being investigated predicts added nutrient response. The best extractant will have most of the points in the lower left (Cate-Nelson graphic technique) and in the upper right quadrants. The vertical dividing line between quadrants is the critical level, the soil test below which response to added nutrient is very likely. The horizontal line approximately separates those trials with a statistically significant response from those with a nonsignificant response.

II. SOIL TEST CALIBRATION

Soil test calibration is the process of ascertaining the meaning of the soil test measurement in terms of crop response (Bray, 1936, 1937; Olson et al., 1958; Corey, 1987; Rouse, 1967). The purpose of soil test calibration is to describe the soil test results in easily understood terminology and to simplify the process of making fertilizer recommendations by placing soils in response categories. The terminology often used to describe categories is very low, low, medium, high, and very high concentration ranges.

A. Continuous Curves

A common procedure used in establishing soil test categories is to plot relative yield or yields vs. soil test and fit a continuous curve to the points. The curve is then divided into several categories such as low, medium, and high or it is divided into fertility indices (Cope & Rouse, 1973). The basis for the division into classes is subjective and arbitrary since continuous regression models have no inflection point as a justification for making a division.

B. Probability Approach

The Cate-Nelson correlation procedure, described in a previous section, has a fundamental advantage. In addition to showing whether there is a good correlation, it also separates soil response data into two populations, those likely to respond and those unlikely to respond to specific nutrient additions. The soil test value where this split occurs is known as the soil test critical level (Fig. 4-3). Soils testing below this level usually respond to added nutrient and those testing above this level usually do not respond to added nutrient. This fundamental separation recognizes the basic fact that a soil test cannot predict yield or the absolute amount of response. A soil test can only be used to determine the probability that a response will occur (Fitts, 1955; Fitts & Nelson, 1956). Cate and Nelson (1971) also developed a simple statistical procedure for partitioning soil test data into two classes.

The next step is to divide the soil test data into more than two categories (Fitts, 1955; Olson et al., 1954, 1958) if there are sufficient field data to permit more separations. If three categories are used, one could be a *low* category where the probability of a response is great and the amount of fertilizer recommended is large, a *medium* category where there is a 50% probability of getting a response, and a *high* category where there is a small probability of a response. None or only a small amount of starter fertilizer is recommended on soils in the high category.

When using the Cate-Nelson procedure, for example, the medium category could bracket the critical level. Soil test levels below this could be called low (response to applied fertilizer likely) and soil test levels above this could be called high (response to applied fertilizer unlikely). An alternative would be the Cate-Nelson Analysis of Variance Method (Nelson & Anderson, 1977). This statistical procedure can be used to establish three or more classes.

As more data are obtained, more soil test categories can be established. Many soil testing laboratories use five categories or more. Also, as more data are obtained categories can be established for peculiar soils and each crop. The main purpose of soil test categories is to convert the soil test numbers or indices into terms that will give a grower some indication of the nutrient status of his soil.

Another reason for establishing soil test categories is to simplify the fertilizer recommendation process when laboratory staff use tables in making fertilizer recommendations for growers. However, at present most recommendations are made from equations in computers. As a result, simplification for staff efficiency and accuracy is no longer a major concern.

III. SOIL TEST RECOMMENDATIONS

Given the background of correlation and calibration described and having selected procedural methods that will best serve the soil and other environmental conditions for the area involved, the final step becomes that of interpreting and making recommendations from the specific soil test value. It perhaps goes without saying that the individual making the interpretation should be thoroughly acquainted with the crops and soils of the region for fine tuning the recommendation. As an example, he will know and give recognition to the fact that subsoil of certain soils may be well endowed with nutrient reserves and fail to respond even with a rather low-surface soil test. He will recognize the impact that fallowing will have on certain nutrients and how this will modify the recommendation compared with a continuous cropping situation. He will understand and adjust for the varied responsiveness of different crops to a specified nutrient, give allowance for known allelochemical effects of crop rotation, and potential nutrient sources not measured in the soil test value. In short, the person making recommendations must be well versed in agronomic principles associated with crop production in addition to being a qualified soil chemist.

Inadequate attention to the various local production factors gives rise to some of the observed differences in recommendations coming from different laboratories that have tested the same soil sample. Significant differences in interpretation also come from varied philosophies on what soil test values mean and what fertilization should accomplish.

A. Crop Production Models and Response Curves

A discussion of the processes involved in the development of a soil test would not be complete without examining crop production models and the shape of the curves drawn when plotting yield vs. applied nutrients.

Some have tried to define crop yield by theoretical models such as (1) $Y = F(X_1, X_2, X_3, \dots, X_n)$ (NAS-NRC, 1961) where Y is crop yield and X_i are the factors affecting plant growth. If all of these factors could be measured, predicted, or controlled, the yields of crops could be predicted

accurately by this model. Many factors, however, cannot be measured, predicted, or controlled. Therefore, models using factors that cannot be measured or predicted must be considered as approximations with little or no predictive ability (Passioura, 1973; Perrin, 1976).

The fact a relationship is often found between nutrient level, one of many factors influencing growth, and crop growth indicates soil fertility has an important influence on productivity. It is this relationship that allows soil nutrient extractions to be used as a guide in the fertilization of crops.

The way nutrients influence plant growth is often discussed in conjunction with the shape of a response curve. The discussion usually centers around whether the response is linear or curvilinear.

The linear model was first proposed by Liebig and later broadened by Blackman (1905). It is commonly known as the "Law of the Minimum" and states that yield increases until the minimum factor becomes the factor limiting growth. According to this concept, yield is directly proportional to the amount of the limiting nutrient in the soil.

A curvilinear model was first proposed by Wollny (Gauch, 1972) but later developed by Mitscherlich (1928) and Willcox (1944). This became known as Mitscherlich's Law of Diminishing Returns or simply as the Law of Diminishing Returns. It states that a much larger increase in yield is obtained per unit of applied nutrient when the nutrient is deficient as compared to when that nutrient is nearly adequate. Curvilinear models have been accepted by many, especially for slightly soluble nutrients (Bray, 1963). One point that needs to be recognized about response curves is that when yield data from different sites or years are averaged it always results in a curvilinear response. This would be true even if a linear response were obtained at each individual field trial (Fig. 4-4). In other words, one should be careful when combining data from different experiments to obtain an overall response curve.

While curvilinear crop responses to a nutrient do occur, the way the data are analyzed will strongly influence the conclusions reached. For instance,

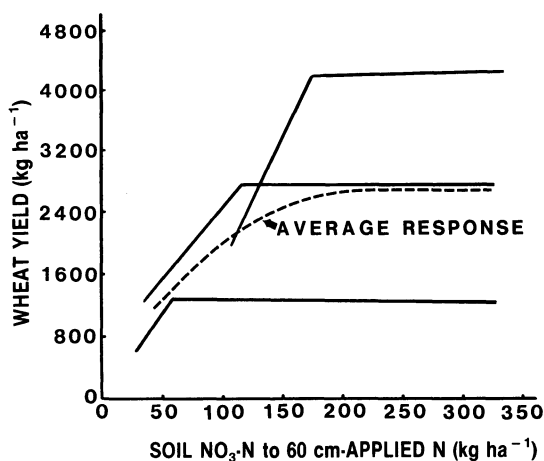


Fig. 4-4. Linear-plateau responses (solid lines) become curvilinear (dashed line) when averaged.

a curvilinear response can be obtained when the data from the replicates of a non-uniform site are averaged even though the response was linear on individual replicates. Another case where response sometimes appears curvilinear is when too few levels of nutrient are applied to adequately define the response (Sparrow, 1979a, b).

Willcox (1949) felt that the more than 27 000 field fertilizer response trials conducted in Germany in the 1930s and reported by Mitscherlich and Gericke gave definite proof that crops respond asymptotically. As indicated above, this is not proof since averaged data from many sites or years always result in an exponential response curve. This again is not to say that curvilinear responses do not occur (Fig. 4-5) but that the occurrence may be less frequent than commonly believed.

Willcox (1949) believed that curvilinear responses (the Mitscherlich equation) only occur when all growing conditions are ideal. The opposite may be more likely. Boyd et al. (1976) and Boyd (1970) presented evidence that curvilinear responses occur because of disease, pests, excess amounts of other nutrients, or other non-ideal situations. Bray (1963) believed crop response to N is linear and response to P and other slightly soluble nutrients is curvilinear. While it is generally agreed that response to N is linear, there are also many examples in the literature of linear response to slightly soluble nutrients, such as P (Boyd et al., 1976; Boyd, 1970; Sparrow, 1979a, b; Waggoner & Norvell, 1979).

Crop response curves can be visualized as a series of curves each with a different maximum or plateau depending on site and year. The potential (maximum) yield is not known and cannot be predicted for any site or year. The plateau or maximum yield on a particular site will be determined largely by soil, crop, weather, and management. Weather is not predictable and many management factors cannot be quantified, therefore the grower is probably most qualified to estimate the plateau or maximum yield (commonly called

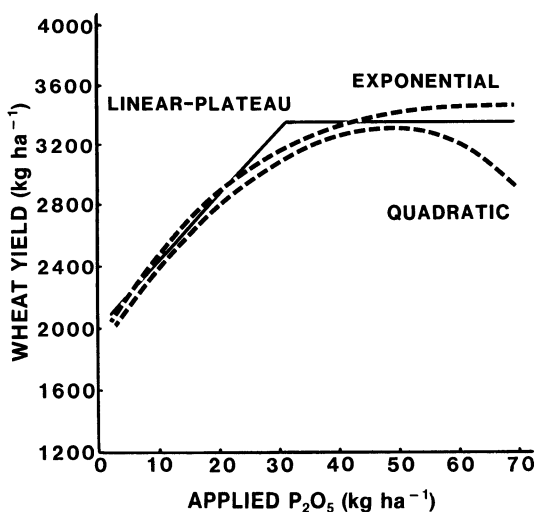


Fig. 4-5. Shapes of plant yield response curves to applied nutrients.

yield goal) for a particular field. The role of the soil testing laboratory then becomes one of determining the amount of nutrient needed in addition to the amount already in the soil so that nutrients are not a limiting factor in reaching the yield goal (Dahnke et al., 1984). Economics alone cannot be used to determine the best fertilizer rate because yield, prices, and the shape of the response curve are not predictable for the coming growing season.

If the response curve cannot be predicted for a given growing season, it follows that the Law of Diminishing Returns or any other curve cannot be used to choose the most economical rate of fertilization. Fertilization rate should be based on soil factors, crop to be grown, and the probability of reaching a certain yield goal. The probability of favorable economics of fertilization is dependent on a well-correlated soil test that has been correctly calibrated and interpreted. In the case of wheat in North Dakota, it takes about 3.7 kg ha^{-1} of N and 0.25 kg ha^{-1} of P to grow an extra 100 kg of wheat (Dahnke et al., 1985). At 1987 prices for hard red spring wheat of \$0.09 per kilogram and N fertilizer of \$0.25 per kilogram of N, a \$5 to \$7 return can be expected for each dollar invested in fertilizer on responsive soils.

B. Examples of Data Interpretation for Making Fertilizer Recommendations

At the present time, there are no established rules to determine what response model is most appropriate to use in the interpretation of fertilizer response data from field trials. Much of the literature on fertilizer response discusses some version of the Law of Diminishing Returns. In this section, several models will be used to interpret the field data from sites 1 to 9 in Table 4-1.

1. Mitscherlich-Bray Function

The observation by some that when equal increments of a nutrient are applied to a crop, the yield response becomes smaller from each increment than from the preceding increment led to various attempts to describe this curvilinear yield response by a mathematical formula. The most famous was that of Mitscherlich (1928) who developed his theory in 1906. Mitscherlich's equation was modified by Bray (1936) to the following form:

$$\log (A - y) = \log A - c_1 b_1 \quad [1]$$

where A is the yield possible when all nutrients are present in adequate quantities; y is the yield when the soil test for nutrient b_1 is less than adequate and c_1 is the proportionality constant.

This equation is sometimes referred to as the *percent yield* equation (Melsted & Peck, 1977) because percentage yield as well as actual yields can be used in the equation (Fig. 4-6 and 4-7). Following is an expanded version of the equation:

Table 4-1. Hard red spring wheat response to applied P fertilizer at several sites in North Dakota.

Site	P test	P ₂ O ₅ applied	Yield	Site	P test	P ₂ O ₅ applied	Yield
		kg ha ⁻¹				kg ha ⁻¹	
1	15	0	1277	8	19	0	2218
		11	1546			11	2490
		22	1680			22	2755
		34	1680			34	3040
		45	1680			45	3293
		67	1814	9	24	0	3369
		0	1344			11	3537
		11	1613			22	3477
		22	1949			45	3779
		34	1983			72	3813
2	4	45	2016	10	19	0	2083
		67	2016			11	2419
		0	1814			22	2890
		11	2016			34	3091
		22	2083			45	3091
3	20	34	2083	11	31	0	1298
		45	2083			22	1231
		67	2285			45	1284
		0	2016			72	1304
		11	2218	12	29	0	3510
4	9	22	2419			22	3618
		34	2520			36	3450
		45	2621	13	28	0	1520
		67	2688			22	1594
5	27	0	2083			45	1594
		11	2285	14	23	0	2609
		22	2554			11	2623
		34	2554			22	2589
		45	2486			45	2589
6	12	0	2150	15	40	72	2576
		11	2285			0	3201
		22	2486			18	3201
		34	2554			30	3416
		45	2554			42	3248
7	8	0	2150	16	32	54	3302
		11	2418			0	4970
		22	2688			120	4593
		34	2957			240	5084
		45	2957				

$$\log (A - y) = \log A - c_1 b_1 - cx \text{ (Melsted \& Peck, 1977)} \quad [2]$$

where c is the efficiency factor for applied fertilizer and x is the quantity of fertilizer needed. This equation is meant to be used to determine the amount of fertilizer needed to raise the percent yield from one point to another. Figure 4-7 indicates that it will take approximately 18 kg ha⁻¹ of P₂O₅ to increase the yield from 95% of maximum to 98%. Using the wheat yield data in Table

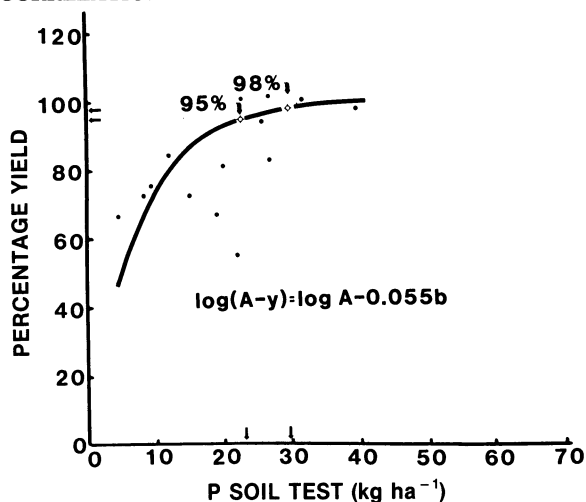


Fig. 4-6. The Mitscherlich-Bray function relating P soil test level to percentage yield of wheat.

4-1, this would be equal to increasing the yield by 114 kg ha^{-1} of wheat. This points out one of the frequent criticisms of the Mitscherlich—Bray function and other curvilinear models. They recommend too much fertilizer in relation to the amount of yield increase obtained at or near maximum yield.

2. Other Curvilinear Models

a. Yield Response. Another method of interpreting field data for fertilizer recommendations is to plot yield response vs. amount of applied nutrient (Hauser, 1973). The data are first grouped according to the soil test categories established by soil test calibration. In this case, the data from Table

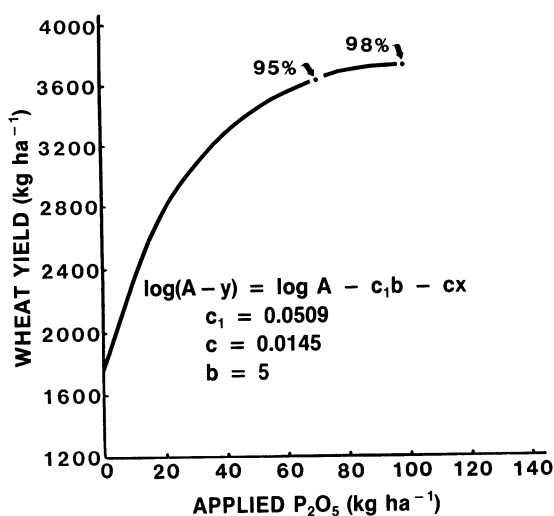


Fig. 4-7. The Mitscherlich-Bray function relating applied P_2O_5 to wheat yield at a soil test of 5 kg ha^{-1} by the Olsen test.

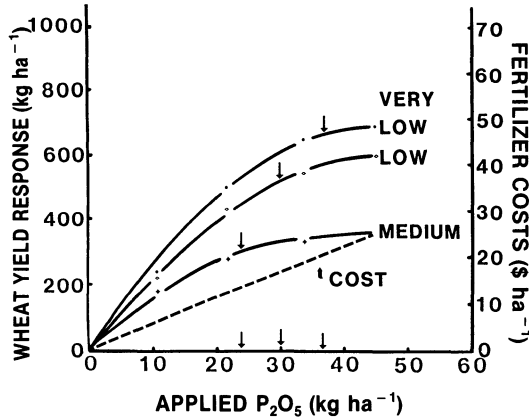


Fig. 4-8. Interpretation graph showing the relationship between wheat response to applied P for three soil test levels.

4-1 are grouped into very low (0-10 kg of P ha⁻¹), low (11-21 kg of P ha⁻¹) and medium (22-34 kg of P ha⁻¹) categories. The average yield response for trials in each of these categories is then plotted against the amount of applied nutrient (Fig. 4-8). The most economical rate of fertilizer application is determined by plotting cost of applied fertilizer on the same graph (Fig. 4-8). The optimum fertilizer rate is the point on the curve where marginal revenue equals marginal cost. The major advantage of this method is simplicity. The fact that the resulting recommendations have no relation to total yield is a disadvantage.

b. Yield. Another procedure for soil test interpretation is to use curvilinear regression to express yield as a function of soil test and applied fertilizer. This method is usually unsatisfactory because yield is determined by many factors other than the nutrient variable (Colwell, 1967). As with the Mitscherlich equation, which is similar to this method, the fertilizer recom-

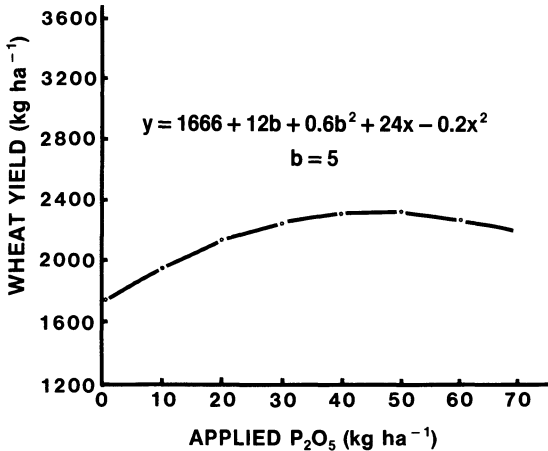


Fig. 4-9. Combining yield data from all sites using curvilinear regression.

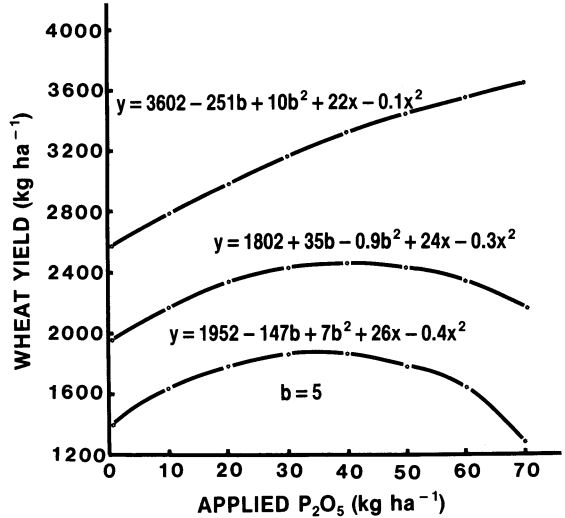


Fig. 4-10. Using curvilinear regression after the data was separated into three different yield levels.

mendation increases rapidly in relation to yield increase near the point of maximum yield (Fig. 4-9). The other point evident with this method is that a very small portion of the yield range of sites 1 to 9 (Table 4-1) is represented by the resulting curve (Fig. 4-9). A greater portion of the yield range can be taken into consideration by placing the data into high, medium, and low yield groups (Fig. 4-10). Note that the amount of applied P₂O₅ needed to reach maximum yield increases from the lowest yielding group to the highest yielding group (Fig. 4-10). The next obvious step would be to look at the yield response curves for individual sites (Fig. 4-11), which leads to the following method of soil test interpretation.

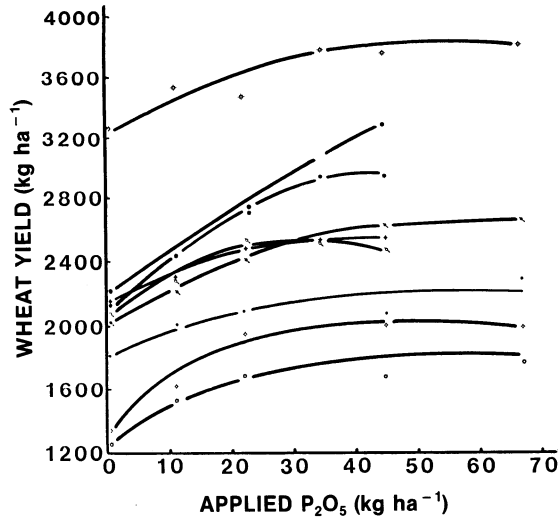


Fig. 4-11. Wheat yield response to P data from each site represented by smooth hand fitted curves.

Table 4-2. Hard red spring wheat response to applied N fertilizer at several sites in North Dakota.

Site	Soil NO ₃ -N to 60 cm + applied N	Yield
	kg ha ⁻¹	
1	84	2218
	106	2554
	129	2554
	151	2621
2	30	1142
	58	1814
	86	2150
	114	2688
3	142	2621
	99	1814
	155	3562
	211	3965
4	267	4368
	323	4032
	110	2554
	166	3427
5	222	3763
	278	3763
	334	3629
	34	806
6	56	1277
	78	1277
	101	1277
	60	1277
	83	1747
	105	1882
	128	1882

3. Plateau Yield Points

In a previous section it was mentioned that although many prefer to represent response data with continuous curves, in many cases a response can be as well represented by a linear-plateau curve. This is true for both-soluble and slightly soluble nutrients in the soil. The phosphate response data from the first nine sites in Table 4-1 are plotted and the points fitted using continuous curves in Fig. 4-11 and linear-plateau curves in Fig. 4-12. The same comparison is made using N response data (Table 4-2) in Fig. 4-13 and Fig. 4-14. In both cases, linear-plateau curves fit the data as well or better than a continuous curve. The linear-plateau curve has the advantage of more readily indicating the point at which maximum yield is reached.

Since yields often increase linearly to the point of near maximum yield, it is logical from an economic point of view to fertilize to this point. A line drawn through the plateau-yield points (Table 4-3, Fig. 4-12) can, therefore, represent the fertilizer recommendations that should be made for various yield goals on, in this case, P-deficient soils. The following equation represents the line through the plateau-yield points in Fig. 4-12:

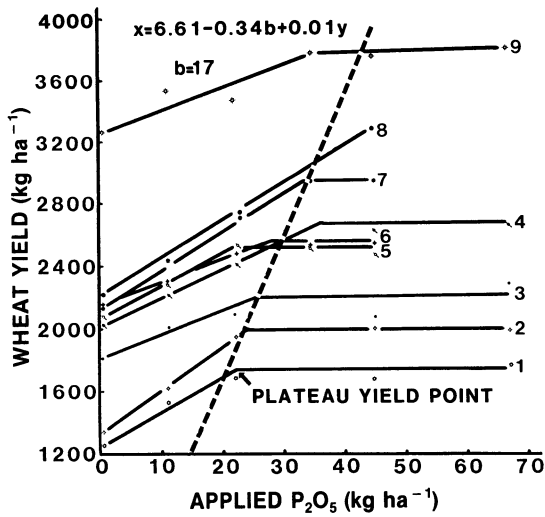


Fig. 4-12. Wheat yield response to P data from each site represented by hand fitted linear-plateau curves with a line drawn through plateau yield points.

$$x = 6.61 - 0.34b + 0.01 y \tag{3}$$

where x is kg ha⁻¹ of P₂O₅ recommended, b is P soil test, and y is yield goal.

Recognizing that the relationship between soil test level and yield is tenuous because of the fact that soil fertility is only one of many factors influencing yield, the line through the plateau yield points is assigned a soil test value near or slightly below the critical level (Fig. 4-3). The area to the right of this line represents more responsive sites (a lower soil test) whereas the area to the left represents less responsive sites (Fig. 4-15). The final step

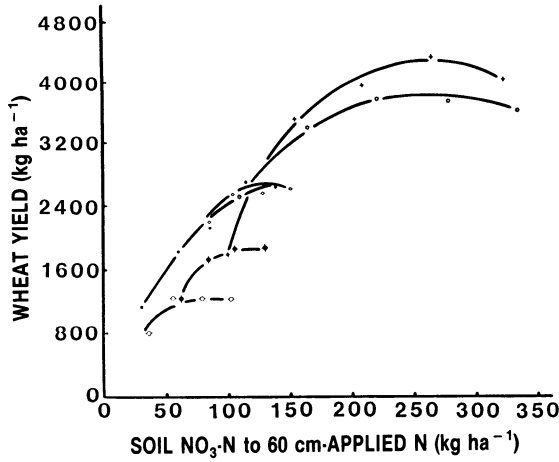


Fig. 4-13. Wheat yield response to N data from each site represented by smooth hand fitted curves.

Table 4-3. Soil tests and plateau yields for nine hard red spring wheat field trials in North Dakota.

Site	P soil test	Plateau yield	Applied P ₂ O ₅ for plateau yield
		kg ha ⁻¹	
1	15	1750	22
2	4	2000	24
3	20	2200	26
4	9	2680	37
5	27	2550	23
6	12	2580	28
7	8	2960	35
8	19	3300	45
9	24	3780	35

is to write an equation for the nutrient recommendation using soil test and the grower’s yield goal. In this example, the recommendation equation for the very low, low, and medium testing fields in Fig. 4-15 is:

$$x = y (0.0163 - 0.0003b) \tag{4}$$

where *x* is the recommendation in kg ha⁻¹ of P₂O₅, *y* is the yield goal of the grower in kg ha⁻¹ and *b* is the soil test.

4. Comparison of Interpretation Methods

A comparison of the recommendations for some of the methods discussed above is shown in Fig. 4-16. These recommendations were all developed using the same data and demonstrate how much fertilizer recommendations vary for near maximum yield depending on the methods used to interpret the data. Figure 4-16 clearly shows that for near-maximum yield

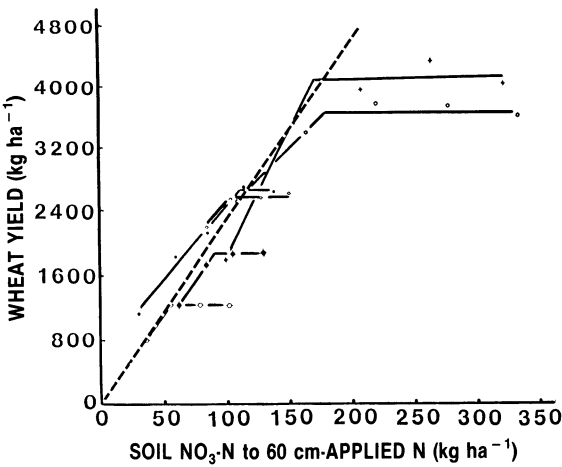


Fig. 4-14. Wheat yield response to N data from each site represented by hand fitted linear-plateau curves with a line drawn through plateau yield points.

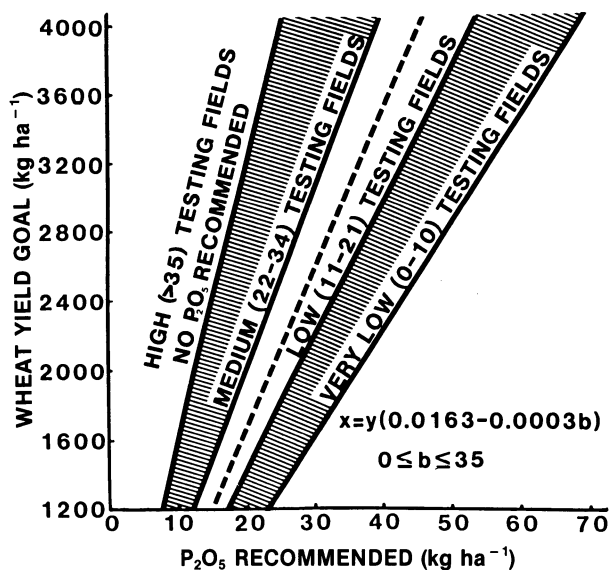


Fig. 4-15. Very low, low, medium, and high soil test recommendations made using the Plateau Yield method. The dashed line through the middle of the low testing category represents the plateau yield points of Fig. 4-12.

the Mitcherlich method makes the highest recommendations. It also shows the Yield Response method makes recommendations that do not change much as soil test changes. The Plateau Yield method recommends about half as much P at a very low test level as the Mitscherlich method.

The method of drawing a line through the Plateau Yield or maximum yield points has also been used with N response data for wheat (Table 4-3 and Fig. 4-14) and potato (Table 4-4 and Fig. 4-17) in North Dakota.

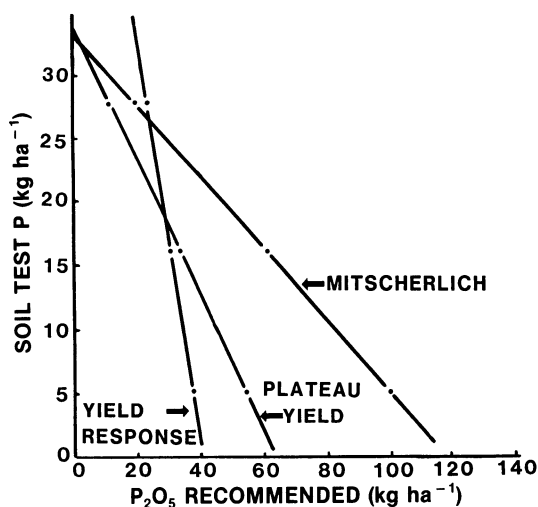


Fig. 4-16. Comparison of P recommendations from three different methods of soil test data interpretation.

Table 4-4. Potato response to applied N fertilizer at several sites in North Dakota.

Site	Soil NO ₃ -N to 60 cm + applied N	Yield
	kg ha ⁻¹	t ha ⁻¹
1	56	20.8
	84	24.6
	112	24.4
	168	22.0
2	56	24.6
	84	27.1
	112	26.8
	168	26.2
3	32	16.7
	59	18.3
	87	22.2
	143	22.4
4	56	28.2
	84	28.8
	112	30.4
	168	29.0
5	56	31.4
	84	32.1
	112	35.2
	168	33.4
6	26	18.7
	82	27.8
	138	31.1
	194	30.8
	250	32.6

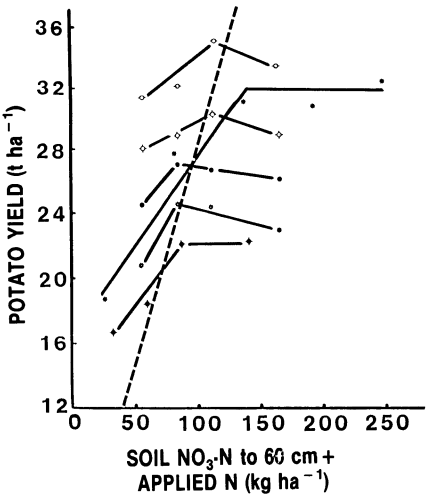


Fig. 4-17. Line representing plateau yield points of potato response to applied N.

The Plateau Yield data interpretation method is different from other methods in that no attempt is made to make recommendations from an average response curve. Recommendations are made from a line that represents the average plateau yield points of responsive sites. In essence, whether the yield response curve is linear or curvilinear is of little importance because only plateau yield points are used in developing the recommendations.

C. Cation Saturation Ratio

A series of reports during the 1940s and 1950s proposed ideal proportions of the major exchangeable cations in soil (Bear et al., 1945; Bear & Toth, 1948; Graham, 1959). The proposed ranges were 65 to 75% Ca^{2+} , about 10% Mg^{2+} , 2.5 to 5% K^{+} , and 10 to 2% H^{+} , or approximate ratios of 7:1 for Ca/Mg, 15:1 for Ca/K, and 3:1 for Mg/K. In contrast to methods just discussed, this method does not use crop response data other than the original work that resulted in the idea.

The above suggests base saturation should be in the range of 80 to 90%. Many other early studies had shown a relation between the percentage saturation of an individual cation and its availability to plants (Allaway, 1945; Chu & Turk, 1949), and that the uptake of a given cation could affect the uptake of other cations (Van Itallie, 1938; York et al., 1954). There was, accordingly, a theoretical basis for the cation saturation ratio concept and it afforded a convenient arithmetic manipulation of analytical data with considerable appeal. As a result, the concept has been in common use by many organizations providing soil testing services and fertilizer recommendations.

It is surprising that the cation saturation concept has received the credibility accorded to it in consideration of other early and recent literature accounts on the issue. Hunter and associates in New Jersey (Hunter, 1949) could find no ideal Ca/Mg or Ca/K ratios for alfalfa (*Medicago sativa* L.), nor did Foy and Barber (1958) find yield response of corn (*Zea mays* L.) to varying K/Mg ratio in Indiana. Similar Ohio studies of alfalfa and German millet (*Setaria italica* L. Beauv.) revealed no yield effects from varied Ca/Mg ratios (McLean & Carbonell, 1972), nor were any Mg or K responses obtained with corn on four Nebraska soils having widely varying ratios of Ca/K, Ca/Mg, and Mg/K (Olson et al., 1982). Neither was the concept of any value in predicting K response of crops grown on coastal plain soils of Delaware (Liebhardt, 1981). Perhaps the most comprehensive study refuting the concept is that of McLean and associates (Eckert & McLean, 1981; McLean et al., 1983) where varied levels of Ca, Mg, and K relative to each other were employed in a complete factorial design with crops in both growth chamber and field experiments. They concluded the ratio had essentially no impact on yields except at extremely wide ratios where a deficiency of one element was caused by excesses of others. They emphasized the need for assuring sufficient levels of each cation rather than attempting adjustment to an ideal cation saturation ratio that does not exist.

D. Implications of Interpretation

1. Surface vs. Profile Soil Testing

Sampling only surface soils has been traditional in soil testing for the obvious reasons that a major portion of crop root systems exist there and surface samples are easy to collect. There is mounting evidence, however, of the need for collecting and analyzing samples from as much of the crop rooting profile as possible (Murdock & Engelbert, 1958; Herron et al., 1971; Reuss & Rao, 1971; Hill et al., 1978; Leggett, 1959; Soper & Huang, 1963; Young et al., 1967). The need applies especially for very soluble nutrients like $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ and most particularly for the drier cropping regions where drainage through the rooting profile rarely occurs. Residual mineral N in the rooting profile has, however, proved to be a dominant factor in irrigated agriculture controlling rate of fertilizer N required for optimum production of corn (Olson et al., 1976; Herron et al., 1971) and sugar-beet (*Beta vulgaris* L.) (Reuss & Rao, 1971). This suggests that profile mineral N is a factor as well for crop production in humid climatic regions with deep, medium to fine-textured and well-drained soils.

Deep rooted long growing season crops like corn and sugarbeets are capable of using residual N to depths of at least 180 cm so long as deep moisture is available and the upper profile does not contain abundant available N (Gass et al., 1971; Peterson et al., 1979). Taking into consideration the use of deep residual N by the crop to be grown will reduce the amount that ultimately could become a groundwater contaminant.

Subsoil reserves of slightly soluble nutrients like P and K can also control response to fertilizers containing those nutrients whatever the surface soil test value may be (Murdock & Engelbert, 1958; Olson et al., 1985). Some laboratories adjust fertilizer recommendations in accordance with known subsoil nutrient status of specific soil series without actually analyzing subsoil samples.

2. Rapid Build-up and Maintenance

The rapid build-up and maintenance concept of fertilization promotes the application of sufficiently high rates of deficient slightly soluble nutrients, like P or K, to raise the soil test level in 1 or 2 yr. This is followed by an annual application equivalent to the amount likely to be removed by the crop to be grown. The intention is that the farmer will be protected against any possible yield loss because of nutrient deficiency. This is a common approach to soil test interpretation and crop fertilization. When combined with the cation balance concept or the Mitscherlich equation, fertilizer rates can become quite liberal.

Trade journals are filled with reports justifying higher fertilizer rates for building and maintaining soil fertility while achieving maximum economic yields, even to the extent of advocating that the soil test never be allowed to drop to the point where crop response to applied fertilizer occurs. It is difficult to find any documentation in the literature of long-term, appropri-

ately designed experiments that economically justify maintenance above the critical level. The rapid build-up and maintenance concept discounts the inherent nutrient delivery capacity of a soil's native mineral reserves, which with most soils other than sands is large for most nutrients. It is these native reserves that allow the non-eroded soil of the Morrow Plots to produce corn yields of more than 3000 kg ha⁻¹ after 100 yr and more than 5000 kg ha⁻¹ when rotated with soybean [*Glycine max* (L.) Merr.] in both cases with no fertilizer applied (Welch, 1976). Further, if the maintenance aspect of this concept of fertilization were to follow its precepts, there would need to be a recommendation for replacement of all 13 soil-derived nutrients likely to be taken up in the projected crop yield and not just N, P, and K. Complete adherence to this system of interpretation would essentially eliminate the need for further soil testing from the nutrient standpoint once the initial build-up had been accomplished. It has its most logical application for soil regions depleted in surface soil nutrients and essentially devoid of inherent subsoil nutrient reserves, such as the most highly weathered soils of warm and humid regions with high nutrient-fixing capacities (Yost et al., 1979).

3. Sufficiency Level

The sufficiency approach to soil test interpretation is similar to the rapid build-up and maintenance with the following exceptions:

1. The rate of build-up of the soil fertility level is much slower.
2. The soil fertility level is built to a much lower level.

Test results are classified low, medium, and high with associated probabilities of yield response to applied fertilizer (McLean, 1977; Olsen et al., 1954; Bray & Kurtz, 1945; Olson et al., 1954; Cope & Rouse, 1973; Dahnke, 1985; Cate & Nelson, 1965). The high or very high category, being above the level of yield response, receives no fertilizer recommendation. The medium category receives a small recommendation because responses are infrequent in this category. Fields in the low category receive more fertilizer because the soil's supply is not adequate. The actual amount recommended on medium testing fields is usually more or less equal to maintenance recommendation. The amount of fertilizer recommended on very low testing fields often is more than maintenance, resulting in a slow build-up in the soil. Most of the research establishing the efficacy of soil testing has focused on these calibration ranges, and the majority of university laboratories retain this system.

The sufficiency level approach is the most conservative among the three systems under consideration. Whereas the cation ratio and the rapid build-up and maintenance level concepts center on fertilizing the soil, the sufficiency level concept emphasizes different cut off levels for different crops.

There is no basis for a belief that sufficiency level interpretation procedures result in soil mining. Fertilizing most soils at nominal rates in accordance with likelihood of crop response still provides a gradual buildup of soil test values to a sufficiency level (Olson et al., 1982; Havlin et al., 1984; Cope, 1981; McLean, 1977; Mattingly, 1973). Yost et al. (1979) found on an oxisol total yield and P uptake were similar after four crops of corn

for periodic broadcast and annual band treatments in which the same total amount of P had been applied. This indicates that even on oxisols, which are capable of precipitating large amounts of P, the sufficiency approach may be a better approach than the build-up and maintenance approach.

4. Economic and Environmental Implications

The interpretations made from soil tests have an immediate economic impact on the farmer as well as long-term agronomic and environmental impacts. In the first case, it goes without saying that the farmer's economic interests are best served by achieving the highest yield possible under his cropping conditions with the least amount of fertilizer. These criteria are not being met by many soil testing programs at the present time, probably because of the rapid build-up and maintenance concept of interpretation used by those laboratories. Rapid build-up and maintenance programs simply do not fit with economics for the majority of temperate region soils for reasons already elaborated. Its use should probably be restricted to very highly weathered soils high in sesquioxide and 1:1 type clays.

Long-term agronomic damage can result from excessive applications of certain nutrients related to plant physiological disturbances at the plant root surface and elsewhere within plant structures. One of the more commonly observed interactions of this kind is P-induced Zn deficiency. It can be readily corrected by applying Zn fertilizer, but possibly at unnecessary cost to the farmer. More serious is the induction of Fe deficiency, particularly on high pH soils, with overuse of P and Zn. Another type of excess is the toxicities to crops that can result from overuse, especially from continued applications of Cu and B. Crop removal of excess Cu can be a long process.

Finally, soil test interpretations that result in overly liberal fertilizer applications can have environmental impacts for which agricultural producers will be condemned by the rest of society. Contamination of streams, lakes, and groundwaters by nutrients and pesticides is occurring with increasing frequency causing public concern. No one appreciates the eutrophication of surface waters heavily committed to recreational use, nor is the presence of any foreign material in drinking water acceptable to the average citizen.

There is no question that soil erosion and nutrient runoff has contributed to eutrophication of surface waters or that fertilizer N is responsible for some groundwater nitrate. It seems logical that a major role of soil testing from this point onward should be one of assisting with the control of nutrient pollution in the environment (Ellis & Olson, 1986).

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Chapter 5

Soil pH and Lime Requirement Determination

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A potentiometrically determined soil pH is essentially an index of hydrogen ion (H^+) activity in solution at equilibrium with soil particles. However, H^+ activity is not the only factor contributing to the potential developed by a glass/calomel electrode combination in the presence of soil particles. Soil pH is, nonetheless, a measure of the intensity of acidity or alkalinity and is used in deciding whether a soil needs liming or acidification. While soil pH may not be a thermodynamically well-defined test, it is useful for the following reasons: soil pH determination is relatively rapid, precise, and inexpensive; values are easily interpreted and relatively well understood; and soil pH is broadly related to the availability of some elements that are required by, or are toxic to plants.

Mineral soils that have pH¹ values below 4 contain free acids generally arising from the oxidation of S or S-containing compounds. Furthermore, soils that have values below about pH 5.5 likely contain exchangeable Al that may be present at sufficiently high levels to be toxic to plants (Thomas, 1967; Hoyt & Nyborg, 1971a). These soils may also contain toxic levels of Mn (Adams & Wear, 1957; Morris, 1948; Ouellette & Dessureaux, 1958; Foy, 1964). Although it is possible to find soils with a pH below 7 that contain unreacted limestone (free carbonates), it is difficult to predict from soil pH values when soils start accumulating large quantities. Past experience suggests that at pH 7.2 soils will occasionally contain sufficient carbonates to neutralize the acid in the Bray-1 P-extracting solution (25 cmol_c L⁻¹ soil; Bray & Kurtz, 1945). In any event, soils with a pH situated between 7.0 and 8.5 contain free carbonates. Higher pH values, up to 9.9, are occasionally encountered in soils from semiarid and arid regions. These contain, in addition to free limestone, varying amounts of carbonates and bicarbonates of alkali metals, commonly Na.

Soil pH is an intensity measurement of soil acidity or alkalinity, and as such, does not indicate the amount H or hydroxyl ions present. An analogy for the intensity parameter is air pressure in a container. Although, pres-

¹Unless otherwise indicated soil pH refers to measurements made in water.

sure is proportionally related to the amount of air in containers of uniform size, pressure alone does not indicate the quantity of air present in containers of different volumes. Similarly, pH can indicate the amount of acidity present in soils with identical cation-exchange properties. However, pH does not indicate the amount of acidity or free-carbonates present in soils with differing cation-exchange properties. For example, a coarse-textured soil containing little organic matter (OM) (low cation-exchange capacity, CEC) with a pH of 4.0 may have a lime requirement of only 1 t ha^{-1} for attaining pH 6.5, while a fine-textured soil having the same pH and containing a high OM level may require 25 t to achieve the same pH. Similarly, alkaline soils may contain greatly different amounts of free carbonates at identical pH levels.

It is interesting that the term *neutral* soil is frequently used, but has no precise meaning. Strictly speaking, a soil with a pH of 7.0 has an equivalent activity of H and hydroxyl ions in solution at equilibrium with soil particles as found in freshly distilled water. However, distilled water at equilibrium with the 0.03% carbon dioxide (CO_2) in the atmosphere will have a pH value of about 5.7. Soil air contains from 10 to 100 times more CO_2 (Bradfield, 1941). Accordingly, water at equilibrium with these higher CO_2 levels can have pH values situated between about 5.7 and 4.5. As soil neutrality is undefined, why do we wish to raise the pH of acid soils to between 6.5 and 7.0? Precise reasons may not exist, and justifications are probably rooted in early concepts of soil chemistry. The relatively low cost of liming to a pH between 6.5 to 7.0 in many places may have influenced the common supposition that liming to that level is desirable for efficient crop production.

Generally, soils with a pH around 7.0 have a better supply of bases and possibly other plant nutrients than those that have been leached to a lower pH level. However, it may be erroneous to conclude, as Adams and Pearson (1967) pointed out, that soil-supplied plant nutrients become more available to plants by liming acid (leached) soils to a pH near 6.5 or 7.0. Similarly, Woodruff (1967) stated that pH values recommended by most agencies are far above those required by plants to produce optimum yields. Current agronomic thinking appears to favor the concept that acid soils be limed to a sufficiently high pH to suppress Al and Mn toxicity and, thereby, allow crops to achieve optimum yields. However, a large proportion of soils will continue to be limed to around pH 6.5 where liming costs for achieving or maintaining that standard are relatively low, because it has gained widespread acceptance.

Soil pH is a measure of the intensity of soil acidity (or alkalinity) but does not reveal the amount that will react with limestone when raising pH to a desired level. Buffer-pH lime requirement (LR) tests have been developed for estimating the amount of limestone required by a plow layer of soil (a weight or volume contained in a defined area) to achieve a desired pH. In fact, the LR of a soil is defined as the rate of liming material required by a plow layer to raise its pH to a specified value (Soil Science Society of America, 1987). A LR is a capacity index of soil acidity as it assesses the amount to neutralize for achieving a desired pH. Soil tests are also available for determining whether soils contain plant-toxic levels of Al or Mn and

so decide whether liming is needed (Hoyt & Nyborg, 1971a, b, 1987). However, if levels are found to be sufficiently high to affect plant growth, a buffer-pH method is then used to determine the LR to raise pH sufficiently to neutralize toxic elements.

As indicated by Schollenberger and Simon (1945), the amount of H displaced from soil colloids depends on the final pH of a soil at equilibrium. Effectively, as pH is raised, successive amounts of covalently held H^+ are displaced from exchange sites for reaction with dissolved limestone. Accordingly, LR increases with increasing target pH; though it is difficult to accurately measure a LR to achieve a pH much above 6.5, presumably because free carbonates start accumulating in some soils around this pH.

Hydrogen ions are not released directly from permanent exchange sites located on mineral soil colloids for reaction with dissolved limestone (Schofield, 1949; Coleman et al., 1959; Pratt & Bair, 1962). According to this definition, exchangeable ions are held by pH independent electrostatic linkages. Hydrogen is often said, therefore, to be nonexchangeable. Nonetheless, H^+ is released by soil colloids when increasing pH by liming; this occurs through two pathways mainly. The first is hydrolysis of Al displaced from permanent exchange sites by increasing soil pH with liming (also of Fe at pH levels below 4 as indicated by McLean, 1982). The Al and Fe so displaced will form metal hydroxides and liberate H^+ for further reaction and neutralization. This source of H^+ is important on very acid mineral soils. The second source of H^+ originates from the dissociation of covalently held H from mineral and organic soil colloids that are progressively released as soil pH increases. Acidity so liberated can be named pH-dependent acidity (from pH-dependent exchange sites). The pH-dependent sites are located on soil OM, possibly allophane, and layer silicate-sesquioxide complexes (Coleman & Thomas, 1964; Schwertmann & Jackson, 1963; Volk & Jackson, 1964). Organic matter is probably the most important source of pH-dependent acidity as suggested by the study of Helling et al. (1964). They found the average contribution of clay and OM to CEC to be about equal at pH 2.5, and that their contribution increased linearly with increasing pH. The contribution of OM, however, increased at a significantly faster rate, being about six times higher than clay at pH 8.0. The increase in CEC is caused by a release of pH-dependent acidity. The latter will react with liming material when increasing soil pH. Of course, neutralization of acidity by liming acid Histosols will, in most instances, largely displace pH-dependent acidity.

Permanent negative exchange sites on mineral soil colloids are countered by metal cations, including Al, which are held by electrostatic forces. The sites are created by isomorphous substitution of cations within the structure of layer silicate minerals by cations of lower charge, thus providing soil colloids with a residual charge (Schofield, 1949; Coleman et al., 1959; Coleman & Thomas, 1967). These exchange sites are called *permanent* because they are present over a relatively wide range of pH values. Permanent sites are considered saturated with bases when positively charged monomeric- and hydroxy-Al have been displaced by other bases, principally Ca or Mg.

As Clark (1965, 1966b) pointed out, there is no consistent relationship between pH and the concentration of soluble Al in soils. Nonetheless, liming acid mineral soils to a pH around 5.5 or above will neutralize Al forms that might contribute to phytotoxicity. This conclusion is suggested by the work of Pratt and Bair (1962), the corrected lime potential data gathered for a wide range of soils by Turner and Clark (1965) and Clark and Nichol (1966), and the work of Coleman and Thomas (1967), Kamprath (1970), and Hoyt and Nyborg (1971a, 1972, 1987). Liming increases soil pH, which in turn causes displacement of Al ions from permanent exchange sites. Displaced Al ions subsequently hydrolyze, polymerize, and eventually precipitate as complex Al-compounds. Crops can tolerate low concentrations of Al as indicated by Adams and Pearson (1967), Kamprath (1970), Evans and Kamprath (1970), and Reeve and Sumner (1970a, b). Presumably, through negating the effect of Al toxicity by liming to a pH of around 5.5, or higher, and by eliminating possible Mn toxicity that might also occur in acid soils (van Lierop et al., 1982), crop yields are no longer limited by the effects of soil acidity.

I. pH DETERMINATION

A. Soil pH Concepts

Sorensen (1909) defined pH as being the negative logarithm of H^+ concentration. This notation has been maintained; though, H^+ potential has replaced concentration to adapt it to electromotive cell thermodynamics. A voltage change of about 59 mV is produced with each 10-fold change in H^+ activity (pH unit). The voltage is defined as zero at pH 7, positive at <7.0 , and negative above that value. The linear relationship between voltage and pH enables a pH meter to interpolate sample values automatically after calibration.

The potential produced by an ideal H or glass electrode follows the relationship predicted by the Nernst equation. The potential increases as H^+ activity increases. Ion activity is defined as the proportion of total ions contributing to a measured potential. However, the activity of a cation cannot be determined independently from its accompanying anion. Activity coefficients, therefore, corresponds to average activity of species present. This difficulty has led the National Bureau of Standards (NBS) in the USA to calibrate and certify buffer standards for an operational pH scale (Bates, 1973; Durst, 1975).

The NBS uses a H and silver silver-chloride electrode combination for defining standards. This combination avoids liquid-junction potential errors. However, the H electrode is cumbersome and unreliable for soil pH determination. Accordingly, soil pH is determined routinely with a glass combined with a calomel reference electrode. It consists of measuring soil-solution emf and comparing it to defined buffer standard values. Accuracy depends on the differences in liquid junction-potential error between standards and sample.

B. Glass Electrode

The glass electrode is sensitive and reversible to H^+ , and is free of oxidation-reduction interferences. However, unlike the H electrode, it has a very high internal resistance. It consists of a thin pH responsive glass bulb fused to a stem of nonresponsive glass. This construction ensures that readings are independent of immersion depth as long as the responsive area is covered with sample. The responsive glass consists of a thin conditioned membrane that allows the potential developed in its gel layer to be reflected to the internal electrode. A silver-chloride electrode immersed in HCl or a buffered chloride solution is commonly used as an internal electrode, though a calomel electrode can also be used.

During the conditioning process, constituent Na^+ and other ions dissolve and leach from the glass forming a matrix of interstices or gel layer. The vacated ion spaces can be filled by H^+ making the bulb selectively responsive to its activity. Entry of H^+ into the gel layer causes these to reflect a corresponding potential to the internal electrode. Porbably not unlike a voltage being impressed across the dielectric of a capacitor. The responsiveness of common glass electrodes is relatively unimpaired by Na^+ and other cations between pH 1 and 9.5 (Bates, 1973). As the pH of most soils fall within this range, it is able to provide accurate pH readings.

C. Glass Electrode Care and Rejuvenation

Accurate soil pH measurement with a glass electrode requires quick exchange of H^+ between hydrated gel layer and sample. As gel-layer water content is related to responsiveness, a glass electrode should not be placed in dehydrating agents. Furthermore, new electrodes or those that have been stored dry should be conditioned before usage by soaking the bulb in water overnight preferably.

Sluggish or impaired electrode performance can be verified simultaneously by noting uncorrected span and response time at calibration. To check span, immerse the electrodes in a first buffer and set the pH meter to its specified value, for instance pH 6.86; rinse the electrodes with distilled water and measure the pH of a second calibration buffer (pH 4.01). The pH meter should be able to provide the second pH without significant slope (percent efficiency) correction. A span correction of around 4% or more suggests that rejuvenation may improve response and accuracy. Response time is examined by determining whether a stable reading is obtained within about 30 s \pm 0.05 pH. If a much longer time is required, the electrode should be examined for cracks; if it is, it should be replaced, if not, it may be rejuvenated.

Glass electrodes are rejuvenated by cleaning, or dissolving and removing a very thin glass layer from the pH-responsive area. Electrode impairment may be caused by a layer of spongy responsive glass having collapsed, or some contaminant sealing the gel layer. Rejuvenation should be started by immersing the tip in about 0.1 M HCl for 15 to 20 s, rinsing with distilled water, and repeating the treatment using a similar concentration of KOH.

The HCl-KOH treatments should be repeated several times. If electrode response is not restored, it may require a more drastic $\text{NH}_4 \cdot \text{HF}$ treatment. However, it dissolves a small amount of surface glass and shortens electrode life. It is accomplished by immersing the pH-sensitive bulb for 30 to 45 s in 20% $\text{NH}_4 \cdot \text{HF}$ contained in a small plastic vessel (it is a hazardous compound). Rapidly rinse the electrode tip in distilled water and dip in about 6 N HCl, followed by another rinsing. Subsequently, set the tip in water, overnight preferably.

D. Reference Electrodes

Hydrogen ion activity is determined with a glass electrode combined with a calomel or silver silver-chloride reference electrode (Bates, 1973). A calomel electrode consists of a platinum element in contact with mercury mercurous-chloride (calomel) surrounded by a KCl solution. The KCl is saturated with calomel and an excess of calomel ensures that it remains saturated with changes in temperature. On the other hand, the silver silver-chloride electrode consists of a silver element coated with a layer of silver-chloride. It is most commonly, like the calomel electrode, surrounded by a KCl solution. However, the surrounding KCl solution in this case is saturated with AgCl. Electrical contact between the calomel (or silver silver-chloride) electrode and test solution is maintained through a salt bridge formed by a small orifice permitting minute KCl flow (the liquid junction). However, the silver silver-chloride electrode can also be used without salt bridge to determine soil pH as shown by Clark (1964, 1966a). This type of electrode is employed by the NBS to define pH standards (Durst, 1975). Its main advantage is that test values are unaffected by liquid-junction potential or suspension effect errors.

A potassium chloride (KCl) concentration can vary a great deal in calomel electrodes without affecting accuracy. Saturated KCl appear to be the preferred concentration in North America; however, 3.5 M KCl seems to be more extensively used in Europe (Bates, 1973). Values measured with either solutions are practically identical because of the comparative nature of pH determination.

According to Willard et al. (1974), the 0.1 and 1.0 M KCl calomel electrodes are more accurate because they reach their equilibrium potential more rapidly and are less affected by changes in temperature than the more concentrated or saturated types. Considering the better properties of the 0.1 M KCl concentration, it is interesting that saturated KCl has almost replaced it (Bates, 1973). This replacement suggests a misunderstanding of the importance of KCl concentration for reliable pH measurements. Presumably, because of the ease of ensuring a constant KCl concentration, has the saturated KCl calomel electrode found preference in North America.

A junction potential error is always present at the liquid junction. Its magnitude cannot be easily established; however, it is generally accepted as being small in solutions. The error consists of a potential produced by an uneven diffusion between K^+ and Cl^- . A more serious source of error in

soils, and colloidal suspensions, is the suspension effect that is additive to the junction potential. A suspension effect is manifested by differences between supernatant, and sediment or suspension pH. Generally, measured pH values decrease from supernatant to suspension.

Although the magnitude of a suspension effect may be more important than junction potential, it is not possible to distinguish between these errors. Whether either or both are caused by a Donnan-type potential produced by a modified mobility of anions relative to cations has not been resolved unequivocally. Nonetheless, these difficulties are associated with soil pH, and have received considerable attention (Loosjes, 1950; Jenny et al., 1960; Coleman et al., 1951; Peech & McDevit, 1951; Peech et al., 1953; Overbeek, 1953; Raupach, 1954, 1957; Bower, 1961; Clark, 1966a; Thomas & Hargrove, 1984) and others.

Peech et al. (1953) and Peech (1965a) suggest that the calomel electrode be placed in the supernatant when routinely measuring soil pH. Although this step may minimize errors, many soils need a 1:2 soil/water ratio instead of the 1:1 Peech (1965a) recommended to obtain sufficient supernatant depth. Even then, supernatants contain suspended colloidal particles. Junction potential and suspension effect errors can only be controlled effectively in two ways: 1, measuring pH in 0.01 *M* CaCl₂ or more concentrated salt solutions (Coleman et al., 1951; Clark, 1966a); or 2, using an Ag-AgCl electrode reference electrode without liquid junction (Clark, 1964, 1966a).

E. Reference Electrode Selection, Care, and Rejuvenation

Although liquid junctions designs vary, they can be classed roughly into four groups according to flow rates. At 50 to 150 $\mu\text{L h}^{-1}$ the ground glass sleeve junction has the fastest KCl flow rate of commercially available electrodes. This junction type is preferred for determining soil pH and buffer pH. However, it can be awkward because the sleeve slips occasionally. Porous ceramic or asbestos fiber junctions may, therefore, be preferred. These have modest flow junctions (5–10 $\mu\text{L h}^{-1}$) and are also recommended for measuring soil pH. Unfortunately, LR buffers have a propensity to diffuse into lower flow junctions. Contamination of electrode solution affects operation and accuracy. Electrodes with very low flow junctions (0.5–3 $\mu\text{L h}^{-1}$; i.e., controlled crack bead junction) and gel-filled electrodes (without KCl flow) are not recommended for soils. These electrodes were designed for applications where higher flow rates are detrimental to the sample.

Electrolyte level should be maintained as high as possible to prevent back-flow and electrode solution contamination. Entrapped air bubbles possibly causing air-locks should be avoided when filling a dry electrode with KCl. The internal solution should be allowed to come to equilibrium after filling before use. Correct sample contact and an operational liquid junction are required for accurate measurements.

A blocked liquid junction is probably the most common calomel electrode problem. Symptoms are sluggish and creeping readings; though these are also present when measuring the pH of poorly buffered samples, partic-

ularly those varying by several pH units and displaying a memory effect. A correctly flowing junction requires regular replenishment of KCl. Operation can be verified with an ohmmeter (note: many digital voltmeters cannot make this test). Fill the electrode with KCl to above the filling hole. Immerse the liquid junction into a small beaker containing sufficient KCl solution of similar concentration. Place one ohmmeter lead tip into the internal solution through the filling hole and the other into the immersing solution. Typically, a resistance of a properly functioning liquid junction varies between 10 to 14 Kohm. An electrode having twice this reading, or more, needs service.

Correct junction operation should be checked when filling, if not daily. A ground-glass and reverse ground-glass sleeve junction is reestablished easily and rapidly by moving the sleeve, allowing some KCl to flow out, and firmly reseating the sleeve. The advantage of the reverse sleeve is that it does not fall off the electrode (break) as easily. On the other hand, porous ceramic and asbestos fiber-type junctions can be examined using air pressure applied by squeezing a bulb or plastic KCl filling bottle that seals against the filling hole. This pressure is often successful in demonstrating or re-establishing the liquid junction. A minute KCl flow, or a mixture of KCl and fine air bubbles will appear at the tip of a properly functioning junction. The junction of a dry electrode should be moistened by setting it in water overnight. Low flow rate junctions often suffer from blockage by soil particles. Removing the clogged portion of a junction tip may be accomplished by rubbing with waterproof fine emery cloth. This drastic treatment can sometimes repair a reluctant electrode that cannot be rejuvenated otherwise.

II. FACTORS THAT INFLUENCE MEASURED pH

A soil pH is produced by the activity of H^+ in solution to which are added the influence of several other factors. These are discussed under the following subheadings: A. soil/solution ratios, B. soluble salts, C. suspension effect, D. carbonic acid, E. drying, and F. seasonal pH fluctuation. Although discussed separately, many factors are closely interrelated. The objective of this section is to promote standard pH determination procedures, and minimize variations by factors other than changes in H^+ activity. Some verifications were made and regression data included.

A. Soil/Solution Ratios and Sample Size

Hissink (1930), as cited by Peech (1965a), reported adoption of a 1:2.5 ratio which suggest that the importance of a consistent procedure was recognized for achieving comparable results. Early work with potentiometric soil pH determination seemed concerned with moisture contents approaching field conditions. Huberty and Haas (1940) and Chapman et al. (1941) found that soil pH varied from about 0.5 to 1.5 pH with changing moisture contents. Higher moisture contents than necessary for producing a sticky point were required to ensure stable and reproducible results (Chapman et al., 1941).

Similarly, Turner and Nichol (1958) reported that a thinner ratio than 2:1 was necessary to generate reproducible values. More concentrated ratios than the 1:1 recommended by Peech et al. (1947) and Peech (1965a) appear less commonly used; though Jackson (1958) mentions a water saturation percentage and Hesse (1971) expresses preference for a saturated paste moisture content.

A consistent soil/water ratio is important for obtaining reproducible and comparable pH values. However, utilization of low moisture contents which rely on sample appearance (crumbly, sticky point, flow point, and saturated paste) are not advised for the following reasons: 1, moisture content varies with sample texture and OM content; 2, sample preparation is laborious; 3, moisture content is often subjective; 4, low moisture contents aggravate junction potential errors; 5, low moisture contents provide unreliable electrode-solution contact; and 6, electrode malfunction and breakage risk are higher when inserting into a paste.

Probably the most commonly recommended soil/water ratio for determining soil pH is 1:1 w/v (Peech et al., 1947; Peech, 1965a; McLean, 1973, 1982). Using a 20-g soil sample is recommended by Peech et al. (1947), Jackson (1958), and Peech (1965a). Soil pH, measured at a given soil/solution ratio, is not affected by sample size but may be by electrode position (supernatant, suspension, or sediment). A comparison of the pH of 60 soils determined in 1:1 w/v (Y; weighed samples) and 1:1 v/v (X; scooped) soil/water ratios ranged from 3.59 to 8.81 (Y), and 3.56 to 8.79 (X) with means of 6.28 and 6.25, respectively ($Y = 1.01X + 0.05$; $r = 0.999^{**}$, significant at $P = 0.01$; $s_{y,x} = 0.06$), revealed that weighing was unnecessary for precise pH measurement, as similar regression parameters were obtained between procedures and replicates of a procedure.

Using a 1:1 ratio usually provides sufficient supernatant to measure pH when using 20-g samples. However, slurries or pastes are often produced at this ratio when soils contain high clay or OM levels. A 1:2 ratio is probably more practical for routine pH determination when soils have a wide range in properties. Average pH generally increases somewhat by diluting soils from 1:1 to 1:2 ratio. This was confirmed by also determining the pH of 60 soils mentioned earlier at a 1:2 ratio. Values ranged from pH 3.56 to 8.79 with a mean of 6.25, and 3.64 to 9.11 with a mean of 6.39 for 1:1 and 1:2 (v/v) soil/water ratios, respectively. Although average pH increased slightly, differences were small enough to justify not using different interpretative norms: ($Y = 1.00X + 0.05$; $r = 0.999^{**}$; $s_{y,x} = 0.07$). Data was gathered with a ground-glass sleeve junction reference and a glass electrode combination.

Soil pH measurement in 0.01 M CaCl₂ relies on a 1:2 soil/solution ratio (Jackson, 1958; Peech, 1965a; Hesse, 1971) originally recommended by Schofield and Taylor (1955). Values are not sensitive to fairly wide changes in soil/solution ratio (Schofield & Taylor, 1955; Turner & Nichol, 1968; Clark, 1964; Rytí, 1965; White, 1969). It is unnecessary, therefore, to weigh soil samples for pH determination when using this solution. Puri and Asghar (1938) reported using soil/1 N KCl ratios ranging from 1:2.5 to 1:25 and found little effect on the pH of acid, but a significant effect on that of cal-

careous soils. Jackson (1958) and Hesse (1971) recommend using a 1:2.5 w/v soil/1 *N* KCl ratio. Collins et al. (1970) used a 1:2 soil/1 *N* KCl ratio. Little, if any, dilution effect was reported between pH measurements made at 1:1 and 1:2 ratios with 0.01 *M* CaCl₂ and 1 *N* KCl for mineral and Histosols by van Lierop and Tran (1979) and van Lierop (1981a), respectively.

1. Recommendation

A 1:2 or 1:2.5 v/v soil/solution ratio is suggested for determining pH of soils with a wide range of properties whether using water, 0.01 *M* CaCl₂, or 1 *N* KCl as the suspending solution. Changing a soil/solution ratio over a narrow range does not affect pH values for interpretative purposes. Accordingly, weighing soils is not generally justifiable for routine pH measurement. The ratio and suspending medium used should be specified when reporting results.

B. Soluble Salts and Lime Potential

The increase in pH produced by diluting soils from a 1:1 to a 1:2 soil/solution ratio is not directly related to acid dilution, but is caused by a decrease in H^+ dissociation with lower solution ionic strength. This conclusion is based on lime-potential findings which demonstrate that by adjusting pH for changes in activity of Ca and Mg in solution (the predominant cations in most acid soils) a remarkably constant value results (Schofield & Taylor, 1955). It was coined the lime potential and defined as being: $pH - \frac{1}{2}p(Ca + Mg)$. Effectively, in its nonlogarithmic form, the lime potential bears a readily recognizable kinship to the ratio law of Schofield (1947) $[H^+/(Ca^{2+} + Mg^{2+})^{1/2}]$. Soil pH and $\frac{1}{2}p(Ca + Mg)$ increase in value with dilution but their difference, the lime potential, remains constant over a relatively wide range of ratios and electrolyte concentrations. The constancy of the lime potential has been confirmed when Ca and Mg activity are determined (Turner & Nichol, 1958, 1962; Clark, 1964). The lime potential may also fluctuate less seasonally as it corrects for changes in solution salt content. In any event, a relatively dilution-independent pH value is obtained by measuring in 0.01 *M* CaCl₂, though there is little point in routinely subtracting 1.14 ($\frac{1}{2}pCa$ in 0.01 *M* CaCl₂) from measured values as Thomas (1967) pointed out. The constancy of the lime potential appears desirable, however, determining $\frac{1}{2}p(Ca + Mg)$ is onerous and difficult to justify for a routine interpretative index of soil acidity.

The difference in pH between water and 0.01 *M* CaCl₂ measurements is often assumed to be about 0.5 pH unit. Although that may be a good average value, actual disparity varies from zero (similar values) to more than a pH unit, depending on soil salt content. Generally, pH differences decrease as salt content increases. The effect of salt level on pH divergence is suggested by lime-potential findings. However, the effect of salt concentration on the disparity between water and 0.01 *M* CaCl₂ pH values was also clearly demonstrated by Rytí (1965).

The effect of solution ion level on the size of discrepancy between water and 0.01 *M* CaCl₂ pH was verified by contrasting values of 30 relatively low-salt soils with conductivities ≤ 0.1 dS m⁻¹ (1:2 v/v soil-water extracts) against those of a second group of soils with higher conductivities situated between 0.1 and 8 dS m⁻¹. Regression parameters derived between pH values from low-salt soils measured in water (Y; 1:2 v/v ratio; range = 4.49–8.52; $y = 6.34$) and 0.01 *M* CaCl₂ (X; 1:2 v/v ratio; range = 3.63–7.69; $x = 5.54$) produced the following: $Y = 0.99X + 0.83$; $r = 0.99^{**}$; $s_{y,x} = 0.21$. On the other hand, regression parameters from high-salt soils pH were different: (Y; 1:2 v/v soil/water ratio; range = 4.13–9.48; $y = 6.77$) and 0.01 *M* CaCl₂ (X; 1:2 v/v ratio; range = 4.18–8.34; $x = 6.30$): $Y = 1.086X - 0.07$; $r = 0.97^{**}$; $s_{y,x} = 0.34$. The difference between these regression parameters emphasizes the role of solution ionic level on the disparity between water and 0.01 *M* CaCl₂ pH values.

Correcting for salt content by entering extract conductivity as a second variable in fitting a multiple linear-regression equation decreased the standard error of estimate ($s_{y,x}$) from 0.34 to 0.23. Addition of solution conductivity as a contributing variable significantly improved the precision of the regression equation for predicting water from 0.1 *M* CaCl₂ pH values.

Lower pH generally results from using 1 *N* KCl instead of water. Puri and Asghar (1938) found that values were about 1.5 pH unit lower. However, results reported by Collins et al. (1970), van Lierop and Tran (1979), and van Lierop (1981a) suggest that the disparity is closer to a pH unit with acid low-salt soils. Values in 1 *N* KCl are generally lower than in 0.01 *M* CaCl₂; however, it is not uncommon to see little difference or the reverse with calcareous soils. The reason for a smaller difference or reversal with calcareous soils was thought to be related to a change in predominant cations on dissolution of soil carbonates.

Differences between water and 1 *N* KCl pH values are affected by salt levels as well as pH. The latter was suggested by the slope of a regression equation fitted between pH data of 40 soils measured in water (Y; 1:2 v/v ratio; range = 3.90–8.88; $y = 6.85$) and 1 *N* KCl (X; 1:2 v/v ratio; range = 3.40–8.05; $x = 6.02$): $Y = 0.86X + 1.70$; $r = 0.97^{**}$; $s_{y,x} = 0.28$. The slope suggests that pH disparity decreases with increasing soil pH.

1. Recommendations

The principal advantage in determining soil pH in 0.01 *M* CaCl₂ or 1 *N* KCl is that values are independent of electrode position (no suspension effect). As with measurements made in water, samples need not be weighed, as narrow changes in soil/solution ratios have little effect on pH. Values measured in 0.01 *M* CaCl₂, or 1 *N* KCl should rely on another interpretative scale as suggested by Davies (1971). Water, 0.01 *M* CaCl₂, and 1 *N* KCl values are closely correlated with reported coefficients situated between $r \approx 0.97^{**}$ and 0.99^{**} (Ryti, 1965; Collins et al., 1970; Davies, 1971; van Lierop, 1981a).

C. Junction Potential

It is assumed that a suspension effect is an aggravated junction potential caused by impeded mobility of K^+ relative to Cl^+ by large electrostatically charged soil colloids. Synonymous usage of these errors is made in this section. Refer to section I.D for an introduction to its mechanism.

The theory that attributes junction potential to a Donnan emf generated by an impeded mobility of K^+ relative to Cl^- was developed by Overbeek (1953). Experimental results supporting it were obtained by Coleman et al. (1951), Bloksma (1957), and Bower (1961). The suspension effect is illustrated by van Olphen (1963) who relates that by keeping the salt bridge of a first calomel electrode in the supernatant and that of another in the sediment a Donnan potential is observed. Marshall (1964), as cited by Thomas and Hargrove (1984), attributed this potential difference to a Donnan potential caused by a higher H^+ activity in the solution in proximity of the sediment relative to the supernatant. If such were the case, substituting two glass electrodes for the calomel units should result in a potential difference. Such a potential has not been reported.

Generally, suspension pH is lower than supernatant pH. Peech et al. (1953) indicate that junction potentials rarely exceed 0.25 pH unit. They and Peech (1965a) suggest that the liquid junction be located in the supernatant after precipitation of soil particles when measuring pH. Unfortunately, obtaining a clear supernatant usually takes considerably longer than allocated for measuring pH. Its absence means that the size of the suspension effect can be as high as reported in the literature. Maximum values of 0.9 and 0.5 pH unit were reported for mineral soils by Coleman et al. (1951) and Rytí (1965), respectively. Similarly, high values of 1.1 pH unit were observed with acid Histosols by van Lierop and MacKenzie (1977). The magnitude of the suspension effect can vary from being negligible to over a pH unit, and appears to be largely influenced by soil salt content. Coleman et al. (1951) reported that soil pH in 1 *N* KCl remained unaffected by electrode position in the sample. Clark (1966a) reported finding no suspension effect when salt content was higher than 0.005 *M* $CaCl_2$.

Strangely, a negative junction potential was reported by Peech et al. (1953) as being caused by a change in the nature of the predominant cations. Rytí (1965) also reported higher suspension than supernatant pH for a soil with a pH above 7.0. Similarly, Raupach (1954) reports suspension pH values that are as much as 1.4 pH unit higher than supernatant values for soils with $pH \geq 7.0$.

The pH of many calcareous soils increases when stirring a supernatant into a suspension of soil particles. This anomalous suspension effect, however, may be attributed to rash acceptance of an apparently steady value. Readings of reluctant calcareous soils may require up to 30 min to settle to near-equilibrium value. Slow stabilization is probably not just related to low H^+ activity, but appears attributable to low sample buffering. The reverse suspension effect observed with the verification in this study was thought to be produced by an absence of equilibrium pH, because similar reverse sus-

pension effects were observed with soils suspended in 0.01 *M* CaCl₂, 1 *N* KCl, and 2 *N* NaCl. It is generally accepted that suspension effects are absent when measuring pH in salt solutions. This suggested that weak sample buffering was responsible for a slow response time, hence anomalous suspension effect. Clark (1964) has indicated that to determine pH of calcareous soils accurately may be difficult.

The time needed for measuring pH of calcareous soils can be reduced to that required for acid soils by swirling soil/solution mixtures with a magnetic stirrer. Considerable hysteresis can be experienced when measuring pH of a calcareous soil without stirring, especially after measuring an acid soil. Initially, pH readings creep relatively rapidly when changing to a weakly buffered calcareous soil; however, the rate of pH change slows after the first minutes, and a rash reading is easily accepted because it seems stable compared to acid soils. Yet, it can be in error by as much as 1.5 pH unit.

1. Recommendations

Soil pH measurements in 0.01 *M* CaCl₂ or 1 *N* KCl are free of suspension effect errors. Values are thus independent of electrode position. Calcareous soil/solution mixtures should be stirred during pH determination.

D. Effect of Carbon Dioxide on Soil pH

The pH of distilled water at equilibrium with carbonic acid at partial pressure of 0.03% CO₂ (pCO₂) in the atmosphere is about 5.72 (Bradfield, 1941). However, a soil atmosphere contains much higher pCO₂ pressures than the air above it. This increase is largely a result of soil biological activity and restricted soil ventilation. Bradfield (1941) suggests that soils contain from 10 to 100 times more CO₂ than the atmosphere above it, and values as high as 12% CO₂ have been proposed (Simmons, 1939). Higher pCO₂ pressures impose higher soil-solution carbonic and bicarbonic acid contents. In turn, these higher contents lower soil pH and increase the concentration of Ca and Mg in solution (Simmons, 1939; Whitney & Gardner, 1943; Turner & Clark, 1956).

The effect of pCO₂ pressures on soil pH have been studied mostly with calcareous soils. Whitney and Gardner (1943) report changes between 1 and 2.5 pH units by increasing the pCO₂ a 100-fold. Although, the change in pH can be predicted from pCO₂ pressures and the solubility product constant of calcareous material, these vary in different soils, and free carbonates are often more soluble than calcite (Cole, 1957; Doner & Pratt, 1969; Olsen & Watanabe, 1959; Clark, 1964). Increasing pCO₂ pressures also affect pH of noncalcareous near-neutral soils (Nichol & Turner, 1957); increasing pCO₂ pressure by a 100-fold, decreased soil pH by about one unit. The effect of CO₂ variation on acid soil pH has not been as extensively studied; however, it can be assumed from lime-potential findings that increasing carbonic and bicarbonic acid concentrations increases Ca and Mg concentrations in solution. These increases, decrease soil pH.

1. Recommendation

Although $p\text{CO}_2$ changes can affect soil pH significantly, air- or oven-drying samples reduces $p\text{CO}_2$ pressures to that in the atmosphere. As the $p\text{CO}_2$ pressure in the atmosphere can be considered constant, drying samples before analysis should eliminate the effect of variable $p\text{CO}_2$ on soil pH.

E. Effect of Drying on Soil pH

Soils are usually dried, crushed, and sieved before analysis. Baver (1927) reported a decrease between 0 and 0.6 pH by air drying. Bailey (1932) concluded that pH was generally lowered somewhat by air drying. Similarly, Huberty and Haas (1940) and Collins et al. (1970) found that oven drying decreased pH further. Bowser and Leat (1958) also observed that pH decreased an average of about 0.4 pH unit with drying, but noted that it increased with a calcareous soil. Average decreases of 0.15 and 0.5 pH unit were reported for drying acid Histosols by Davis and Lawton (1947) and van Lierop and MacKenzie (1977), respectively.

Interestingly, the decrease in pH with drying appears reversible. Comparing pH values of 100 acid and calcareous soils measured 1 d after adding water and 7 d later indicated that average pH increased by about 0.25 unit. The increase was assumed to be related to reducing conditions produced by saturating soils. Although, little precise information is available concerning the causes of acidity fluctuation with drying or wetting soils, its reversible nature suggests that oxidation and reduction of S compounds have an important role. In any event, drying-wetting cycles promote OM mineralization, and eventually produce a salt effect on soil pH. However, drying soils before analysis provides a constant soil/solution ratio when measuring pH, hence less dilution of soil salts, and a lower pH with higher salt.

The decrease in pH with drying can be quite important in soils containing large amounts of sulfides. Hesse (1971) mentions changes of 2 pH units between the wet and dry season in an East Pakistan soil. Greater changes can be observed on acid sulfate clays (often called *cat-clays* or *mud-clays*) from around pH 7 when flooded to pH 2 during the dry season (Moormann, 1963; Dost, 1973; Bohn et al., 1985). The oxidation of S compounds are largely responsible for such wide variations in pH, though the oxidation of Fe compounds and hydrolyses of Al and Fe have important roles.

1. Recommendation

It is recommended that soils be air or oven dried before determining pH. Drying affects soil pH, but changes are not generally agronomically significant unless soils contain large amounts of sulfides. Wide changes in pH, however, can result from drying soils containing sufficient oxidizable S compounds. Whether pH of these soils is determined on field-moist or dried samples, or both, depends on the objectives of the tests.

F. Seasonal pH Fluctuation

In view of the many factors that affect soil pH during the growing season, it is not surprising that it fluctuates during the year and from year to year. Bayer (1927) and Huberty and Haas (1940) noted that pH varied about a unit during the growing season and that variations seemed related to prevailing moisture regime. Bowser and Leat (1958) found that pH varied by as much as 2 units during the growing season on a calcareous soil, and that moisture and pH fluctuations appeared interrelated. Generally, pH gradually increases and decreases during periods of high and low rainfall, respectively (van der Paauw, 1962). Although, fluctuations of field-moist soils may be partially attributable to changes in soil atmosphere $p\text{CO}_2$ pressure during periods of high biological activity, low pH tends to occur during summer months when moisture levels are often lower and presumably soil aeration is better. In any event, drying soils, before pH determination, reduces the effect of $p\text{CO}_2$ to a homogeneous value, yet pH fluctuations are observed on air- or oven-dried soils. The pH of acid Histosols varies like that of mineral soils (van Lierop & MacKenzie, 1977). They reported variations up to 1 pH unit on limed but only 0.2 units on unlimed treatments with field-moist samples. Their findings support the assumption that variations in carbonic acid concentrations are implicated in pH fluctuations of field-moist samples. Be that as it may, the principal factors contributing to pH fluctuations have been discussed under drying and salt effects. The importance of soil-solution salt content on pH fluctuation was confirmed by Collins et al. (1970).

1. Recommendations

Seasonal fluctuation indicates that pH is a changing soil property. Many factors affect its value. Fluctuation is an integrated response to all components contributing to pH value during a period. If anything, it underlines the desirability of using a uniform and well-documented procedure so that factors other than changes in H^+ activity have a minimal impact. A desirable procedure is precise, rapid, and objective; however, its properties and relationship to other procedures should be known.

III. pH MEASUREMENT

A. Buffer Standards

Certified buffer pH standards can be obtained from the Office of Standard Reference Materials, National Bureau of Standards, Washington, DC, USA 20234. Standards can also be purchased as solutions, tablets, or packets for dissolution from chemical supply houses. They may also be prepared advantageously from high purity chemicals. Adding a preservative consisting of 1 mL of chloroform or toluene, or about 1 g of thymol L^{-1} is recommended to discourage mold growth.

1. KHP Buffer, pH 4.01

Dry potassium hydrogen phthalate (1-KOCOC₆H₄-2-COOH; FW = 204.23) at 110°C for 2 h. Dissolve 10.21 g in distilled water and dilute to 1 L. The pH of this standard is 3.999, 4.002, 4.008, 4.015, and 4.024 at 15, 20, 25, 30, and 35 °C, respectively.

2. Phosphate Buffer, pH 6.86

Dry KH₂PO₄ and Na₂HPO₄ at 110°C for 2 h. Dissolve 3.44 g of KH₂PO₄ and 3.55 g of Na₂HPO₄ in distilled water and dilute to 1 L. The pH of this buffer is 6.900, 6.881, 6.865, 6.853, and 6.844 at 15, 20, 25, 30, and 35 °C, respectively.

3. Borax Buffer, pH 9.18

Dry Na₂B₄O₇·10H₂O at 110°C for 2 h. Dissolve 3.81 g in distilled water and dilute to 1 L. The pH of this standard is 9.276, 9.225, 9.180, 9.139, and 9.102 at 15, 20, 25, 30, and 35 °C, respectively.

B. pH-Meter Calibration

Use pH 6.86 and 4.01 buffer standards for calibration and verification if few calcareous soils are present. However, a pH 9.18 buffer should be added to check operational span when a significant proportion of calcareous soils are tested.

As many different types of pH meters are in use, only general calibration principles can be described. Exact steps are provided in the operation manual supplied with the pH meter. Generally, calibration should emulate the following approach. Set average operating temperature (usually 25 °C). Insert electrodes in the pH 6.86 buffer standard, gently swirl buffer, and set value when reading has stabilized using the calibration control. Subsequently, rinse electrodes with distilled water and insert into pH 4.01 buffer while swirling gently: a stable reading can be adjusted using the slope (percent efficiency) correction. If a slope correction of about 4% or greater is required see sections I.C and I.E on electrode care and rejuvenation. A calibrated pH meter will read exact standard values without further adjustment. Accuracy should be verified regularly during operation. Electrodes are stored in distilled water when the pH meter is not in use.

C. Measuring pH in Water

1. Procedure

Scoop 10-mL soil samples into appropriate beakers, add 20-mL aliquots of distilled water, and stir thoroughly. Allow the mixture to stand between 15 to 30 min and measure pH. Sluggish calcareous samples should be swirled with a magnetic stirrer to enhance rapid and accurate pH measurement.

D. Measuring pH in 0.01 M CaCl₂

1. Reagents

a. Prepare a 1 M CaCl₂ stock solution (CaCl₂·2H₂O; FW = 147.02) by dissolving 147.02 g in 1 L of distilled water.

b. A 0.01 M CaCl₂ solution is prepared by diluting 10 mL of 1 M CaCl₂ stock solution to 1 L. One liter suffices for 50 samples.

2. Procedure

Scoop 10-mL soil samples into appropriate beakers, add 20-mL aliquots of 0.01 M CaCl₂, and stir thoroughly. Allow the mixture to stand between 15 to 30 min and measure pH. Sluggish calcareous samples should be swirled with a magnetic stirrer to enhance rapid and accurate measurement.

E. Colorimetric Soil pH

Soil pH was determined colorimetrically before pH meters became widely available. The more sensitive indicators and proper technique provide pH values within about 0.3 pH unit of potentiometric values (Davis & Lawton, 1947; Collins et al., 1970; Hesse, 1971). This type of precision is adequate for many applications. Field people often rely on the convenience of these procedures. Information about preparation and use of indicators can be obtained from Jackson (1958), Bates (1973), Woodruff (1961), Peech (1965a), and Hesse (1971).

IV. LIME REQUIREMENT DETERMINATION

A. Introduction

A LR is the amount of limestone (CaCO₃) needed by a plow layer of acid soil to increase its pH to a desired level. The contribution of pH-dependent acidity to LR gradually expands as soil pH is increased. A LR increases, therefore, as a target pH rises. At a pH above about 5.5, the permanent CEC of mineral soil colloids is saturated with bases and no longer contributes to LR.

Rapid buffer-pH LR methods measure a proportion of the acidity neutralized by CaCO₃. The more accurate methods rely on exhaustive displacement (leaching) of acidity to measure LR (Peech, 1965b). Disparity of LR values between various buffer-pH procedures have two principal causes. First, calibration accuracy affects recommendations. Calibration should adjust for incomplete measurement of acidity by a buffer. Second, the discrepancy between soil-buffer and target pH affects the amount and proportion of acidity measured. The buffer's initial pH and buffering capacity also influence equilibrium pH and, consequently, the amount and proportion of acidity included in a measurement.

Accurate LR recommendations depend on three interrelated postulates. First, a buffer-pH procedure should be accurately² calibrated. Accuracy is particularly important for determining the LR of soils with low-buffering capacities as these may be limed (overlimed) with a single application. Second, accurate liming requires uniform application. It also requires that the rate be incorporated in the correct volume or weight of soil. Third, the use of a general liming factor affects accuracy. A factor is often included in recommendations to attempt correction for possible lower reactivity of commercial limestone relative to finely ground CaCO_3 used to calibrate or verify a method. An arbitrary general factor may not be justified as limestone solubility is related to its nature and grinding fineness.

Space restrictions allow only a partial presentation of the many methods in use; an overview of operational assumptions and relative accuracy for the principal procedures has, however, been included. Three buffer-pH methods with updated calibrations are advanced, though others are referenced and can be used effectively. The three methods were selected because they are well known, relatively simple to use, and versatile.

B. Lime Requirement: Volume or Weight Basis?

Buffer-pH LR determination methods are calibrated or verified with liming rates expressed in meq CaCO_3 100 g^{-1} or mL^{-1} of soil. More recently, LR rates have been reported in $\text{cmol}_c \text{ kg}^{-1}$, which are equivalent SI units. The LR calibrations for the proposed procedures are in metric tonnes of CaCO_3 2 million L^{-1} of soil (a furrow-layer of 1 ha to a depth of 20 cm). These are equivalent in magnitude to $\text{cmol}_c \text{ L}^{-1}$ soil. Corresponding rates in tons acre^{-1} to 20-cm depth are derived by multiplying recommendations by 0.45. The merits and drawbacks of various approaches of calculating LR are discussed by van Lierop (1989).

C. Shoemaker, McLean, and Pratt Procedure

1. Principles

The Shoemaker, McLean, and Pratt (SMP) (Shoemaker et al., 1961) single-buffer procedure has been widely adopted and found particularly accurate for soils needing more than 8 to 10 t limestone ha^{-1} (McLean et al., 1966, 1978; Tran & van Lierop, 1981a, 1982). It has often been described as more sensitive to acidic Al than the Woodruff buffer (McLean et al., 1960, 1964, 1966; Shoemaker et al., 1961; Pionke et al., 1968). A greater sensitivity was assumed to be the reason for the better accuracy of the SMP buffer at higher LR values. However, it should then also be more precise² as high LR soils generally contain larger amounts of acidic Al. The SMP buffer is consistently as closely correlated with reference LR values as the Woodruff, which suggests that it responds to the same forms of acidity (McLean et al.,

² A procedure is accurate when measured and true values agree. It is precise when measured values are reproducible and proportionately related to true values.

1960, 1966, 1978; Pionke et al., 1968; Webber et al., 1977; Fox, 1980; Tran & van Lierop, 1981a, 1982; Loynachan, 1981; Brown & Cisco, 1984; Alabi et al., 1986).

Similar correlation coefficients between reference LR and soil-buffer pH values suggest that the SMP and Woodruff buffers are equally precise. This fact and the comparison of corresponding accuracy zones (i.e., the Woodruff is relatively accurate at low LR but recommends too little for high LR soils while the SMP buffer recommends too high LR when soils require low levels but is relatively accurate for high LR) suggest two particularly important conclusions. First, the dissimilar accuracy between zones is probably not related to inherent differences between buffers, but rather to corresponding calibration procedures. Although, Shoemaker et al. (1961) did not describe the procedure used for calibrating the SMP buffer, they apparently employed a regression method for relating soil-buffer pH to reference LR values. This procedure is considered largely responsible for its greater accuracy at higher LR's. The second conclusion suggested by the relative accuracy zones is that the relationship between soil-buffer pH and LR, unlike between buffer pH and additions of strong acid, is not linear but curvilinear (Fig. 5-1).

Curvilinearity between soil-buffer pH and LR values increases with increasing difference between initial buffer and target pH (desired soil pH; Tran & van Lierop, 1981a, 1982). The principal reason for curvilinearity is that buffer-pH procedures measure a greater proportion of soil acidity from low than high LR soils. Conversely, linearity is optimized by using similar initial buffer and target pH. Superfluous pH-dependent acidity is measured when soil-buffer pH is higher than target pH.

Curvilinearity between incubation and measured LR values was indicated by the data of Loynachan (1981) for the SMP and Woodruff buffers. It was also suggested by the data of Webber et al. (1977), and the discussion of Alabi et al. (1986). Furthermore, it was confirmed by Nõmmik (1983) and

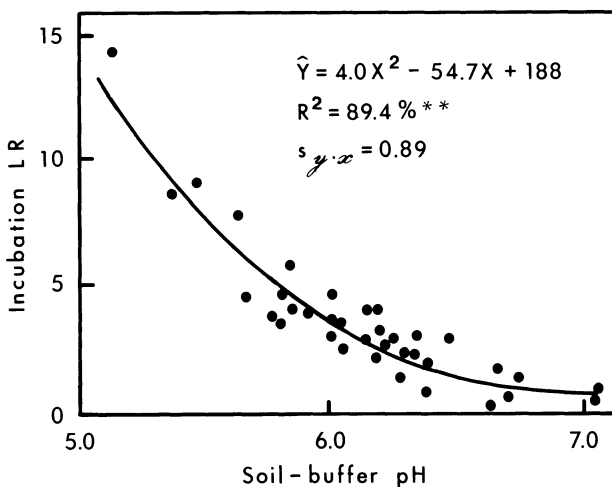


Fig. 5-1. Curvilinear relationship between soil-buffer pH and LR values to attain pH 5.5 for the SMP buffer. (From Tran & van Lierop, 1982.)

Soon and Bates (1986). A double-buffer procedure tends largely to correct for curvilinearity by inter- or extrapolating a desired change in soil pH against a calibrated change in soil-buffer pH. In any event, the accuracy of the SMP single-buffer procedure can be improved by using a curvilinear instead of a linear calibration. Curvilinearity is relatively small when target pH is 6.5, but it gradually increases as target pH decreases to 5.5.

McLean was aware that the SMP buffer measured a decreasing proportion of soil acidity as soil-buffer pH values decreased (McLean et al., 1960, 1964, 1966, 1977; McLean, 1973, 1978, 1982). A SMP double-buffer procedure was proposed by McLean et al. (1977, 1978) for improving the accuracy of LR determination of low-exchange capacity soils. However, a single-buffer procedure is more rapid, versatile, and lower in cost. Accordingly, the SMP-buffer calibrations proposed by Shoemaker et al. (1961) and McLean (1973, 1982) were adapted for curvilinearity by combining calibrations with those obtained by Tran and van Lierop (1981a, 1982) to improve accuracy at low LR values and for achieving soil pH values of 5.5, 6.0, 6.5, and 7.0. Calibrations are in metric tonnes of CaCO_3 2-million L^{-1} of soil (1 ha to a depth of 20 cm): see section IV.B for modifying rates to fit other measurement units.

2. Equipment and Reagents

1. pH meter equipped with a glass and ground-glass junction reference electrode.
2. Standard buffers, pH 6.86 and 4.01.
3. Beakers.
4. Mechanical shaker.
5. Lime requirement buffer.
6. Automatic pipette.
7. A 10-mL scoop soil measure.

3. Shoemaker, McLean, and Pratt Buffer Preparation

1. Ten liters of SMP buffer (500 samples) are prepared by dissolving the following chemicals in about 5 L distilled water while stirring vigorously:
 - a. 18.0 g of *p*-nitrophenol ($\text{NO}_2\text{C}_6\text{H}_4\text{OH}$; FW = 139.11).
 - b. 30.0 g of potassium chromate (K_2CrO_4 ; FW = 194.2).
 - c. 531 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; FW = 147.02).
2. Dissolve 20.0 g of calcium acetate [$(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O}$; FW = 176.19] in about 2 L distilled water.
3. Mix solutions 1 and 2; continue stirring vigorously for about 2 h.
4. Add 100 mL of TEA³ stock solution.
5. Dilute to 10 L and continue stirring for 6 to 8 h.

³Triethanolamine (TEA) stock solution is used because TEA [$\text{N}(\text{CH}_2 \cdot \text{CH}_2\text{OH})_3$; FW = 149.19] is very viscous and difficult to pipette accurately. It is prepared by diluting 280.5 g of TEA ($250 \text{ mL} \cdot 1.122 \text{ g mL}^{-1} = 280.5 \text{ g}$) to 1 L.

Table 5-1. Relationships between soil-SMP-buffer pH and lime requirement (LR) values to achieve pH 5.5, 6.0, 6.5, and 7.0 of mineral soils.

Soil-buffer pH	LR†			
	pH 5.5	pH 6.0	pH 6.5	pH 7.0
6.9	0.5	0.6	0.7	0.9
6.8	0.6	1.0	1.2	1.5
6.7	0.7	1.4	1.8	2.2
6.6	0.9	1.8	2.5	2.8
6.5	1.2	2.3	3.3	3.6
6.4	1.6	2.9	4.0	4.4
6.3	2.0	3.5	4.9	5.2
6.2	2.5	4.2	5.7	6.0
6.1	3.1	4.9	6.6	7.0
6.0	3.8	5.6	7.5	8.0
5.9	4.5	6.5	8.5	9.0
5.8	5.3	7.3	9.5	10.0
5.7	6.1	8.2	10.5	11.2
5.6	7.0	9.2	11.6	12.4
5.5	8.0	10.2	12.7	13.6
5.4	9.1	11.3	14.0	14.9
5.3	10.2	12.4	15.0	16.2
5.2	11.4	13.6	16.2	17.6
5.1	12.7	14.8	17.5	19.0
5.0	14.0	16.1	18.8	20.4
4.9	15.5	17.4	20.1	22.0

† Lime requirement in metric tonnes CaCO₃ ha⁻¹ for a furrow layer of 20-cm depth (2 million L) soil.

- 6. Adjust pH to 7.50 ± 0.02 by with either 4 N NaOH or HCl as required.
- 7. Filter buffer through a fiberglass membrane if necessary.

4. Verification

Buffering capacity is checked by titrating 20 mL of SMP buffer from pH 7.50 to 5.00 with 0.1 N HCl. It should be 0.28 ± 0.005 cmol_c HCl/pH. Correctness affects accuracy.

5. Procedure

Measure 10 mL of dry soil samples into beakers (see footnote 4 for a description of volumetric soil measurement). Add 20 mL of SMP buffer, stir with a glass rod to wet samples thoroughly. Shake soil-buffer samples for 15 min at about 200 cycles min⁻¹. Let samples stand an additional 15 min and measure soil-buffer pH. Obtain LR values for desired target pH from Table 5-1 or calculate with equation(s) from Table 5-2.

⁴A volume of soil is measured with a stainless steel cylindrical ladle filled to overflowing by scooping, tapped twice or thrice with a stainless steel rod to eliminate large voids, levelled, and transferred to a beaker. Avoid filling scoop against a side of the container.

Table 5-2. Regression equations relating soil-buffer pH (BpH) to LR values for achieving pH 5.5, 6.0, 6.5, and 7.0 of mineral soils.

Equations†	%R ²	S _{y.x}
<u>LR pH 5.5</u>		
LR(SMP) = 3.498(BpH) ² - 48.77(BpH) + 170.46	99.6	0.33
LR(WDF)‡ = 5.524(BpH) ² - 78.265(BpH) + 277.1	99.7	0.29
LR(MEO) = 1.6(BpH) ² - 25.2(BpH) + 96.3	99.9	0.12
LR(MEH) = 55.1 - 8.86(BpH)	99.9	0.02
<u>LR pH 6.0</u>		
LR(SMP) = 2.573(BpH) ² - 38.76(BpH) + 145.58	99.8	0.25
LR(WDF) = 1.178(BpH) ² - 26.234(BpH) + 124.9	99.8	0.25
LR(MEH) = 75.4 - 11.75(BpH)	99.9	0.02
<u>LR pH 6.5</u>		
LR(SMP) = 1.867(BpH) ² - 31.82(BpH) + 131.23	99.9	0.06
LR(WDF) = -1.063(BpH) ² - 1.156(BpH) + 58.7	99.9	0.09
LR(MEH) = 3(BpH) ² - 47.5(BpH) + 180.2	99.9	0.15
<u>LR pH 7.0</u>		
LR(SMP) = 2.455(BpH) ² - 39.50(BpH) + 156.58	99.9	0.11

† Equations were derived from tabulated data. See corresponding tables for application limits.

‡ WDF, MEO, and MEH represent Woodruff, Mehlich original, and Mehlich-buffer calibrations, respectively.

6. Comments

All buffer-pH procedures extract acidity when initial buffer pH is higher than soil pH. An accurate buffer-pH procedure can estimate a LR within about 0.25 unit of target pH. This tolerance probably approaches the accuracy limitation of the better procedures when used with soils having a wide range of properties. Calculated LR precision should only be expressed to one place after the decimal. Rare instances of soil-buffer pH values above 6.9 are observed on coarse-textured soils that need liming, in such cases recommend a minimum rate. Also see section IV.F.1 for applicable comments.

D. Woodruff Single Buffer Method

1. Principles

Woodruff (1947, 1948) probably acquired his buffer-pH LR test concepts from Brown (1943). His is the first widely used test and has been evaluated many times. The procedure allows rapid and convenient LR determinations. Woodruff (1948) stated that though the quantity indicated by the test was sufficient to bring soil pH to 7.0, heterogeneity of mixing limestone in the field and the presence of slowly reacting larger particles provided the needed insurance that soils would not be completely neutralized. He indicated that the concept of liming soils to a pH around 6.0 to 6.5 was fairly well established and that this buffer would achieve that end.

According to Brown and Cisco (1984), Woodruff produced a new LR determination buffer in the mid-1960s. Though its development is not well

documented, it is discussed nonetheless under section IV.F. It is well to remember that buffer accuracy is imparted by calibration and use, and not particularly composition. Woodruff (1948) stated the following concept concerning measurement of exchange acidity with a buffer: "If the depression in pH is restricted to small values, it is an absolute measure of the exchangeable hydrogen." The effect of buffering capacity on acid-extraction efficiency is supported by buffer-pH experience.

McLean et al. (1960) evaluated the Woodruff buffer and suggested that its accuracy could be improved using regression procedures. McLean et al. (1966) found that it recommended too little for soils with high LR but that it seemed accurate at lower rates. A similar differentiation was encountered between low and high LR soil groups by Tran and van Lierop (1981a). From this differentiation they suggested that the relationship between soil-buffer pH and LR was more accurately described by a curvilinear line.

Webber et al. (1977) evaluated the Woodruff buffer for determining the LR to 5.5 and 6.0 of Canadian soils and found it was as precise as the SMP (Shoemaker et al., 1961) buffer. Loynachan (1981) compared it and the SMP buffer procedure and found that LR values were closely correlated ($r = 0.99^{**}$). However, plotting his Woodruff (or SMP) against incubation LR values indicated a strong curvilinear relationship. A curvilinear relationship was observed for the Woodruff buffer by Tran and van Lierop (1981a, 1982): calibration curvilinearity has been discussed for the SMP-SB procedure and comments are applicable to the Woodruff procedure. Fox (1980) also evaluated the Woodruff procedure and found, like others, that it was as precise as any, that it was quite accurate at low values, but that it underestimated high LR. The Woodruff buffer was also studied by Brown and Cisco (1984) and Alibi et al. (1986) and their findings confirm those of others. The Woodruff buffer is generally evaluated for determining LR to achieve pH 6.5, but Tran and van Lierop (1982) also verified it for determining LR to pH 6.0 and 5.5. They found it as precise as any for pH 6.0, but that it can be a little less precise than some for determining LR to pH 5.5. In conclusion, the original Woodruff buffer calibration is not accurate, improved calibrations derived by Tran and van Lierop (1981a, 1982) are, therefore, provided for determining the LR to pH 5.5, 6.0, and 6.5 for mineral soils. These are in metric tonnes of CaCO_3 2 million L^{-1} of soil (1 ha to a depth of 20 cm): see section IV.B for modifying rates to fit other measurement units.

2. Equipment and Reagents: See section IV.C.2.

3. Preparation of Woodruff (1948) Buffer

1. Ten liters of Woodruff buffer (500 samples) are prepared by dissolving the following chemicals in about 9 L of distilled water while stirring vigorously and diluting to 10 L:
 - a. 80 g of *p*-nitrophenol ($\text{NO}_2\text{C}_6\text{H}_4\text{OH}$; FW = 139.11).
 - b. 6.2 g of magnesium oxide (light MgO ; FW = 40.3).
 - c. 400 g of calcium acetate [$(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O}$; FW = 176.19].
2. Adjust pH to 7.0 by titrating with 4 N NaOH or HCl as required.

Table 5-3. Relationship between soil-buffer pH and lime requirement (LR) values to achieve pH 5.5, 6.0, and 6.5 of mineral soils with the Woodruff buffer.

Soil-buffer pH	LR†		
	pH 5.5	pH 6.0	pH 6.5
6.8	0.3	1.0	1.7
6.7	0.7	2.0	3.3
6.6	1.2	3.1	4.8
6.5	1.8	4.1	6.3
6.4	2.5	5.2	7.8
6.3	3.3	6.4	9.2
6.2	4.2	7.5	10.7
6.1	5.2	8.7	12.1
6.0	6.4	9.9	13.5
5.9	7.6	11.1	14.8
5.8	9.0	12.4	16.2
5.7	10.5	13.6	17.6
5.6	12.0	14.9	18.9
5.5	13.7	16.2	20.2
5.4	15.5	17.6	21.5

† The LR recommendations to achieve pH 5.5, 6.0, and 6.5 were obtained from buffer-pH calibration verifications by Tran and van Lierop (1981a, 1982).

4. Verification

Buffering capacity should be checked by titrating 20 mL of Woodruff buffer from pH 7.0 to 6.0 with 0.1 N HCl. It should be 0.70 ± 0.02 cmol_c HCl/pH.

5. Procedure

Measure 10 mL of dry soil into beakers (see footnote 4 for a description of volumetric soil measurement). Add 20 mL of Woodruff buffer using an automatic pipette. Stir with a glass rod to wet sample thoroughly and allow it to stand for 15 to 30 min. Stir the soil-buffer mixture anew and read pH. Obtain LR values for desired target pH from Table 5-3 or calculate using equation(s) from Table 5-2.

6. **Comments:** See applicable comments in section IV.C.6.

E. Mehlich Single-Buffer Method

1. Principles

Mehlich (1976) calibrated his buffer for assessing the LR to neutralize permanent (neutral-salt) exchangeable acidity (EA). This is the acidity implied in restricting crop growth on acid mineral soils (Kamprath, 1970; Evans & Kamprath, 1970; Reeve & Sumner, 1970a, b; Mehlich, 1976; Mehlich et al., 1976). A curvilinear equation was found necessary to accurately predict

Table 5-4. Relationships between soil-buffer pH and Mehlich lime requirements (LR), and LR values to pH 5.5, 6.0, and 6.5 for mineral soils with the Mehlich buffer.

Soil-buffer pH	Mehlich	LR†		
		pH 5.5	pH 6.0	pH 6.5
6.5	0.4	-2.4	-0.9	-0.6
6.4	0.9	-1.5	0.2	0.3
6.3	0.9	-0.7	1.4	1.2
6.2	1.9	0.2	2.6	2.2
6.1	2.4	1.1	3.8	3.2
6.0	3.0	2.0	4.9	4.3
5.9	3.6	2.9	6.1	5.4
5.8	4.2	3.8	7.3	6.6
5.7	4.9	4.6	8.5	7.9
5.6	5.6	5.5	9.6	9.2
5.5	6.3	6.4	10.8	10.6
5.4	7.1	7.3	12.0	12.0
5.3	7.9	8.2	13.2	13.6
5.2	8.7	9.1	14.4	15.1
5.1	9.6	10.0	15.5	16.7
5.0	10.5	10.9	16.7	18.4
4.9	11.4	11.7	17.9	20.2
4.8	12.4	12.6	19.0	22.0
4.7	13.4	13.5	20.2	23.9
4.6	14.4	14.4	21.4	25.8
4.5	15.5	15.3	22.6	27.8
4.4	16.5	16.2	23.7	29.8
4.3	17.7	17.0	24.9	32.0
4.2	18.8	18.0	26.1	34.1
4.1	20.0	18.8	27.3	36.4
4.0	21.2	19.7	28.4	38.7
3.9	22.5	20.6	29.6	41.0

† Lime requirement calibrations for Mehlich LR values were obtained from Mehlich (1976), to pH 5.5 and 6.0 from Tran and van Lierop (1982), and pH 6.5 by Ssali and Nuwamanya (1981).

LR from buffer-pH values. Calibration of this buffer differs from others in that LR recommendations are meant to produce optimum yields rather than achieve a pH. However, when comparing LR values obtained with its original calibration against incubation values to achieve pH 5.5, Tran and van Lierop (1982) found that it was the most accurate among procedures tested. The probable reason is that neutral-salt EA tends to predominate in acid soils at pH levels lower than 5.5. A remarkable similarity between LR values recommend by Mehlich (1976) and derived by Tran and van Lierop (1982) for attaining pH 5.5 was found, confirming the validity of its original calibration (Table 5-4).

Although, the Mehlich buffer method is precise, its calibration may not be accurate to attain pH 6.0 or 6.5 (Ssali & Nuwamanya, 1981; McLean et al., 1978; Tran & van Lierop, 1981a, 1982). This inaccuracy is expected from using EA values for calibration. This buffer-pH procedure recommends about 50, 59, and 60% of reference values to obtain pH 6.5 (McLean et al., 1978; Tran & van Lierop, 1981a; Ssali & Nuwamanya, 1981, respectively). Nonethe-

less, it is particularly well suited for determining the LR for neutralizing acidity harmful to crop productivity and will generally recommend sufficient limestone to achieve a pH slightly above 5.5. This pH is sufficient to eliminate possible Al toxicity. As LR values to achieve other pH levels may be desired in some instances, calibrations for achieving pH 5.5, 6.0, and 6.5 of mineral soils are provided. Calibrations are in metric tonnes of CaCO_3 2 million L^{-1} of soil (1 ha to a depth of 20 cm): see section IV.B for modifying rates to fit other measurement units.

2. Equipment and Reagents: See section IV.C.2.

3. Preparation of Mehlich Buffer

1. Ten liters of Mehlich buffer (500 samples) are prepared by dissolving the following chemicals in about 7 L of distilled water while stirring vigorously:
 - a. 12.5 mL of glacial acetic acid (CH_3COOH ; FW = 60.05).
 - b. 90 mL of TEA stock solution.³
 - c. 215 g of ammonium chloride (NH_4Cl ; FW = 53.49).
 - d. 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; FW = 244.28).
2. Dissolve 90 g of sodium glycerophosphate, also named sodium salt of beta-glycerophosphoric acid [$(\text{HOCH}_2)_2\text{CHOPO}_3\text{Na}_2 \cdot 5\text{H}_2\text{O}$; FW = 306.12] in about 2 L of distilled water.
3. Mix solutions 1 and 2 while swirling vigorously. Allow it to cool to room temperature, then dilute to 10 L and mix thoroughly.
4. Adjust pH of buffer to 6.60 ± 0.04 with glacial acetic acid or TEA stock solution as required.

4. Verification

Buffering capacity is checked by mixing 20 mL of Mehlich buffer with 10 mL 0.1 N HCl- AlCl_3 solution. The pH of the resulting mixture should be 4.1 ± 0.05 . The 0.1 N HCl- AlCl_3 solution is made by dissolving 4.024 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 mL 0.05 N HCl.

5. Procedure

Measure 10 mL of dry soil into beakers (see footnote 4 for a description of volumetric soil measurement). Add 20 mL of buffer, stir with a glass rod to wet sample thoroughly, allow to stand for 1 h, and measure pH. Obtain LR values for desired target pH from Table 5-4 or calculate using equation(s) from Table 5-2.

6. Comments

Buffer concentration is one-half that advanced by Mehlich (1976) as LR is determined only on selected samples. Negative LR values in Table 5-4 in

dicating that liming is not required. A soil-buffer pH close to 6.6 is occasionally observed with coarse-textured soils needing liming, in such case recommend a minimum rate. See section IV.C.6 for applicable comments.

F. New Woodruff Single-Buffer Method

1. Principles

Mention of the new Woodruff (NW) buffer was made by McLean (1973). It appears to have been developed in the mid-1960s and is described by Brown et al. (1977). According to regression parameters provided by Brown and Cisco (1984) and Alabi et al. (1986), NW buffer is as precise as the original but recommends about 1.6 times higher LR. Given that it provides higher recommendations with the same effective calibration range as the original, suggests that it displaces soil acidity more efficiently, and consequently meets its maximum range more frequently.

According to Brown and Cisco (1984), the NW buffer is more accurate than the original for determining the LR to pH 7.0. They obtained reference LR values, however, by measuring soil pH in salt solutions varying in concentrations between 0.01 to 0.2 M CaCl_2 with a brief $\text{Ca}(\text{OH})_2$ titration to pH 7.0. It is difficult to ascertain whether their conclusion is correct as these procedures affect reference LR values. Regression parameters from Alabi et al. (1986) suggest that the NW-buffer method recommends higher LR values than required to achieve pH 6.5. Recondite as facts may be when comparing results of studies using different methods, an interesting observation is that both studies found that the SMP single-buffer procedure recommended higher values than the NW procedure. The SMP procedure has been shown to overestimate LR of soils with low LR according to McLean et al. (1966, 1978) and Tran and van Lierop (1981a, 1982), inasmuch as low LR soils were preponderantly studied by Brown and Cisco (1984) and Alabi et al. (1986), suggests that NW-buffer LR values are reasonable for low LR soils. Some uncertainty exists, however, as it recommends considerably higher values than the original, which is considered about right for determining low LR soils.

Regression parameters and data reported by Alabi et al. (1986) suggest that the original and the NW (as other procedures) measure a LR when liming is not necessary. This peculiarity is inherent in buffer-pH procedures and emphasizes the need for using soil pH for deciding whether a LR test is required. Buffer-pH procedures occasionally will not indicate a LR on acid soils with low-buffering capacities, and conversely, procedures will occasionally measure a LR for soils with high-buffering capacities when it has a sufficiently high pH (hence does not need liming). This apparent peculiarity is sometimes ascribed to using soils that are different in nature than those originally used to calibrate a procedure. However, buffer-pH procedures rely on measuring a calibrated portion of soil acidity that can react with limestone to achieve a target pH. Such a target pH should preferably be situated be-

tween soil and initial buffer pH. It is hoped that the NW-buffer procedure will be studied further, though, it will give satisfactory results with its calibration.

G. Adams and Evans Single-Buffer Method

1. Principles

The Adams and Evans (A-E) method was developed for measuring the LR of Red-Yellow Podzolic soils (Ultisols) that have low LR and which may be affected by crop yield reduction with overliming (Adams & Evans, 1962). The method was developed because other buffers were not satisfactory for determining the LR of these low-exchange capacity soils. Calibration of the A-E buffer is realized by calculating LR values from a general relationship between soil pH and base *unsaturation*, and the ability of the buffer to indicate the amount of exchange acidity to be neutralized, and hence LR. Inasmuch as the relationship between pH and percent base saturation is known to vary widely with soils (Shaw, 1952), Adam and Evans stated correctly that any general application of such a relationship to soil LR should be made with caution. The difficulty is that percent base saturation and unsaturation are relative intensity terms, while LR is a capacity index of soil acidity. Apparently, calibration values are meant to increase base saturation to 75% and decrease base unsaturation to 25%. These values were shown to correspond to the acidity displaced by ammonium acetate (pH 7.0). Validity of this approach was verified by incubating some soils with increments of $\text{Ca}(\text{OH})_2$ and comparing incubation with estimated LR values. It is interesting to note that Peech (1965b) also reported moderately accurate LR values derived from a generalized pH-base saturation relationship. To such a relationship, Adams and Evans incorporated measured buffer acidity to determine LR to pH 6.5 (Adams & Evans, 1962; Hajek et al., 1972).

According to McLean (1982), the A-E buffer is very sensitive and particularly useful for soils with low LR. It appears to be widely used in the southern USA (Adams, 1984). Furthermore, its accuracy has been verified quite extensively. Fox (1980) evaluated the A-E method and concluded that it tended to overestimate LR, though these were well correlated with incubation values. Similarly, Tran and van Lierop (1981a) found that it was suitable essentially for low LR soils, but that it was not as precise as some for determining higher LR. They also found that the A-E method overestimated LR, and suggested that high initial buffer pH (pH 8.0) could be responsible. Using this initial buffer pH enables the buffer to include pH-dependent acidity between pH 6.5 and 8.0 that need not be neutralized. More recently, Alabi et al. (1986) confirmed that the A-E method overestimated LR of coarse-textured soils. Although it appears to overestimate LR, the A-E calibration includes a liming factor of 1.5. Since most verifications have been carried out either with CaCO_3 or $\text{Ca}(\text{OH})_2$ -incubations without commenting on the liming factor, it may well be responsible for recommending rates above those required to achieve pH 6.5.

H. Nõmmik Single-Buffer Method

1. Principles

The Nõmmik single-buffer method is the most recently introduced buffer-pH LR procedure (Nõmmik, 1983). Relatively little is known about its use or verification. Its buffering components consist of imidazole, maleic acid, and acetate, with K and Na as acidity exchangers. The buffer was developed to enable exchangeable Ca, Mg, and Mn determination in the extract by EDTA titration. Characterizing of soil CEC, in addition to determining LR, may have been a primary goal in developing this procedure as reference LR values to pH 7.0 were used for calibration. These were derived, however, from a single $\text{Ca}(\text{OH})_2$ -incubation treatment (10 wk) by calculating LR values to pH 7.0 by inter- or extrapolation. This procedure assumes a linear relationship between added base and change in pH.

The Nõmmik buffer is probably as precise as any; however, its accuracy is unknown, as perplexing results were reported for a comparison between incubation and values measured with the SMP-SB (McLean, 1973) and Yuan double-buffer methods (Yuan, 1974). Nõmmik measured somewhat higher LR values with the Yuan procedure than indicated by incubation. However, the Yuan procedure does not fully measure incubation LR (McLean et al., 1978; Tran & van Lierop, 1981a, 1982). A difference between the Nõmmik and Yuan procedure is quite possible; however, an incertitude arises because lower LR values were measured with the SMP than by incubation. It is generally recognized that the SMP-SB procedure recommends higher than reference values for soils having low to medium LR's (McLean et al., 1966, 1978; Tran & van Lierop, 1981a; Brown & Cisco, 1984; Alabi et al., 1986).

Nõmmik also found that single-buffer procedures react with proportionately more acidity from low than high LR soils. Curvilinearity was reported for the relationship between soil-buffer pH and incubation LR values by Tran and van Lierop (1981a, 1982), Soon and Bates (1986), the data of Lounachan (1981), and Webber et al. (1977). As indicated for the NW buffer, it is hoped that this procedure will be studied further, though it will give satisfactory results with its current calibration.

I. Double-Buffer Lime Requirement Determination Procedures

1. Principles

Double-buffer LR determination was introduced by Yuan (1974, 1976) and subsequently adapted by McLean et al. (1977, 1978) for use with the SMP buffer. It is said double-buffer procedures differ from single-buffer procedures in that the former weighs the characteristic buffering capacity of a soil to be limed. Be that as it may, it is generally accepted that single-buffer procedures also measure sample-buffering capacity to determine LR. As some confusion about the working mechanism of these procedures arises from these statements, operational principles are developed more explicitly to study differences. It is apparent from diagrams provided that double-buffer

techniques rely on triangulation. However, exact differences between assumptions used for double- and single-buffer methods are not clear from these.

Single- and double-buffer procedures measure the quantity of acidity neutralized by liming to attain a desired pH, which is defined as LR. However, buffer-pH procedures do not measure all the acidity involved (McLean et al., 1977, 1978; Tran & van Lierop, 1981a, 1982). In the case of single-buffer methods, the amount of acidity, and by corollary, the LR to a target pH is determined from the relationship between soil-buffer pH and incubation values preferably established by regression techniques. On the other hand, double-buffer procedures, as originally developed by Yuan (1974, 1976), rely on three fundamental assumptions (operational principles). The first is that changes in soil pH with additions of base or buffer are linear. Second, the change in soil pH produced by adding buffers is extrapolated to the neutralization of soil acidity by CaCO_3 . Third, the buffers completely displace and assess the acidity that is neutralized by limestone. Although none of these fundamental assumptions is entirely correct, their adoption has resulted in the development of precise and relatively accurate LR-determination procedures.

The Yuan and SMP-double-buffer (Yuan, 1974, 1976; McLean et al., 1977, 1978) use the first principle. Its adoption theoretically allows double-buffer procedures to determine LR values to any selected target pH situated between current soil pH and about 6.5 to 7.0. The flexibility of target pH selection appears to be the principal advantage in favor of double-buffer procedures. Single-buffer methods, however, can be calibrated in LR steps of about 0.5 pH unit; these steps satisfy practical needs and may be close to the accuracy resolution of LR-determination procedures in any event. Therefore, the flexibility advantage in favor of double-buffer procedures may be largely apparent. The Yuan- and SMP-double-buffer procedures use the second principle which is usually described as measuring the "individual" buffering capacity of a soil. This measurement relies on inter- or extrapolating the amount of acidity displaced by the buffers, as indicated by their change in pH, into a LR. This principle is usually represented by triangulation diagrams. The third principle is not used by the SMP-double-buffer procedure. McLean et al. (1977, 1978) recognized that buffer procedures displace a proportion instead of the total amount of acidity. They corrected, therefore, for incomplete soil-acidity displacement by multiplying measured values by a constant derived from incubation values using regression techniques.

The main advantage claimed in favor of double-buffer procedures is their greater accuracy at low LR values. This characteristic is especially valuable for avoiding overliming of soils with low-buffering capacities. The SMP-double buffer is more accurate than the Yuan-double buffer procedure for determining higher LR values mainly because it uses a correction factor to adjust for incomplete acidity displacement. It so avoids the large inaccuracies produced by the erroneous assumption associated with the third operational principle. As the only advantage in favor of double-buffer procedures appears to be their greater accuracy at low values, either the Yuan- or SMP-double-buffer procedure can be equally effective.

J. Yuan Double-Buffer Method

1. Principles

The amount of acidity neutralized by CaCO_3 when increasing soil pH is measured in three steps. First, two soil-buffer pH values are determined on different samples with buffers having initial pH values each of 7.0 and 6.0, respectively. Second, the soil-buffering index alpha (α) is derived by calculating the ratio of the amount of acidity displaced relative to the change in pH produced by the buffers. The acidity displaced is calculated from the assumption that 1 cmol_c acidity changes buffer pH by one unit. The change in soil pH produced by the buffers is calculated by subtracting the soil-buffer pH of the pH 6.0 buffer from that obtained with the pH 7.0 buffer. Therefore, α is the slope of a relationship between acidity measured per unit change in pH produced by the buffers. Third, LR is calculated from the slope (α), by extrapolating a desired change in soil pH from that measured with the buffers.

Yuan apparently accepted the operational principles because differences between measured and $\text{Ca}(\text{OH})_2$ -titration LR values were small (Yuan, 1974, 1976). His data suggests that the double-buffer procedure measured an average of about 90% of reference values. McLean et al. (1978) verified the Yuan-double-buffer procedure and found measured LR values too low; this finding was confirmed by Tran and van Lierop (1981a, 1982). The low-measured LR values signify that the third operational principle for double-buffer procedures is incorrect and buffers do not displace all acidity that reacts with CaCO_3 when increasing soil pH to the target value. Tran and van Lierop (1981a, 1982) suggested that the accuracy of the Yuan-double-buffer procedure could be improved substantially by incorporating a correction factor to adjust for the incomplete measurement of soil acidity. They found that the Yuan-double-buffer procedure was as precise as any for determining the LR to pH 6.5 and 6.0, but slightly less precise for 5.5. Fox (1980) evaluated the Yuan- and SMP-double-buffer procedures and also found them about equally precise.

2. Comments

The Yuan-double-buffer method is as precise as any and appears to be quite accurate for determining the LR of poorly buffered soils. Double-buffer LR determination procedures are about twice as costly and time consuming as single-buffer methods. Although these procedures do not require a table or regression equation to relate soil-buffer pH values to LR, calculations are extensive.

K. SMP Double-Buffer Method

1. Principles

The SMP buffer (section IV.C) was adapted by McLean et al. (1977, 1978) to a double-buffer methodology similar to that proposed by Yuan

(1974). This approach was selected for improving the accuracy of LR determination for low-buffering capacity soils. However, the SMP-single buffer does not follow the operating principles used by the Yuan-double buffer procedure exactly. McLean et al. (1977, 1978) tried several procedural variations: they concluded that double buffer, as single-buffer, procedures do not measure all the acidity neutralized by CaCO_3 either. They, therefore, included a proportionality factor into the SMP-double-buffer calibration similar to that needed for single-buffer calibrations. This factor corrects for partial acidity displacement. The proportionality factor is derived from incubation data using regression techniques. Therefore, the SMP-double buffer generally recommends higher LR rates for soils with moderate and high LR levels than the Yuan-double-buffer procedure.

McLean (1982) preferred a double-buffer variation called the single-buffer two-pH technique. It provides essentially the same results as the two-buffer two-pH technique proposed by Yuan (1974) but allows saving in materials and possibly time. McLean (1982) proposed its use for routine LR determination of soils with low-buffering capacities. Indeed this variation lends itself to combine using the SMP-double-buffer modification with the SMP-single-buffer procedure for low LR samples that might benefit from additional accuracy. The one-buffer two-pH technique relies on determining soil-buffer pH for only one sample; rapidly and accurately adding sufficient HCl to the soil-buffer mixture to depress buffer pH to 6.0, and subsequently, after an appropriate reaction period, obtaining the second soil-buffer pH value.

The SMP-double-buffer procedure has been evaluated by several workers over the years (Fox, 1980; Ssali & Nuwamanya, 1981; Tran & van Lierop, 1981a, 1982; Alabi et al., 1986; Soon & Bates, 1986). Generally, it has been found to be as closely correlated with reference LR values as the SMP-single-buffer procedure, suggesting that the procedure is as precise as any. Better accuracy relative the SMP-single-buffer procedure with its original calibration was confirmed for determining LR values to pH 6.5 for low-buffering capacity soils by Tran and van Lierop (1981a). They also found that it was about as accurate as the SMP-single-buffer procedure for determining the LR to achieve pH 6.5 of soils with higher requirements. However, Tran and van Lierop (1982) subsequently discovered that the correction factor proposed by McLean et al. (1977, 1978) did not hold particularly well for determining LR to attain pH 5.5 or 6.0. They found similar inaccuracies associated with the Yuan-double-buffer procedure. Although, confirmation of this finding would be useful, it nonetheless suggests that double-buffer procedures may not be more accurate than single-buffer procedures for measuring the LR to achieve different soil pH levels. Still, the SMP-double-buffer adaptation, like the Yuan-double-buffer procedure, can offer improved accuracy for determining the LR of soils with low-buffering capacities.

2. Comments

See sections IV.C.6, IV.F.1, and IV.I.1 for applicable comments. The SMP-double-buffer procedure has the same disadvantages as the Yuan-double

buffer as it is more onerous than a single buffer procedure. However, the single-buffer two-pH variation can be combined with single buffer methodology for selectively determining LR of soils with low-buffering capacities, which could benefit from double-buffer methodology.

V. INDIRECT LIME REQUIREMENT DETERMINATION METHODS

A. Principles

Indirect LR-determination procedures rely on estimating a LR from soil properties without directly measuring acidity. These methods identify soil components that contribute most importantly to LR. Indirect procedures can be precise but are generally more onerous than buffer-pH procedures. Nonetheless, they are occasionally convenient for determining a LR value from available soil test data. Joret et al. (1934) proposed the following equation relating soil OM and clay content to LR: $0.11 [\% \text{ clay} + (5 \times \% \text{ OM})]$. The relationship suggests that OM contributes about five times more acidity than clay. However, soil clay often exceeds OM content by a factor of 5, and then clay would contribute as much or more to LR as OM. Helling et al. (1964) indicated that soil OM contributes about 2.2 times as much to CEC per gram of material as clay at pH 6.0.

Keeney and Corey (1963) found that clay content or exchangeable Al had relatively little influence on LR. They formulated the following equation relating a desired change in pH and soil OM content to LR: $(\text{pH } 6.5 - \text{soil pH}) \times (\% \text{ OM})$. Organic matter content appears as the principal component in LR for a given change in pH. Keeney and Corey (1963) concluded that their soils contained too little exchangeable Al to influence LR. Presumably because of this, they also found that clay content had little effect. Subsequently, Pionke and Corey (1967) studied the interrelation between acidic Al, clay, and OM contents. They concluded that exchangeable-Al concentration was primarily related to soil pH. They demonstrated that exchangeable-Al concentrations decreased exponentially as soil pH increased and that little or no Al remained at soil pH of about 4.5 (1 N KCl) or above—equivalent to pH of about 5.5 (water). A similar relationship between soil pH and exchangeable-Al concentrations was observed by Thomas (1967), van Lierop et al. (1982), Nõmmik (1983), and others. Aluminum will not generally contribute to LR when soil pH is about 5.5 (water) or above. Accordingly, the equation suggested by Keeney and Corey may be useful for determining LR when soils are between about pH 5.5 and 6.3 (water).

Rémy and Marin-Laflèche (1974) modified the equation proposed by Joret et al. (1934) by adding a change-in-pH factor similar to Keeney and Corey (1963). However, the Rémy and Marin-Laflèche equation retained OM and clay content and emphasizes the role of clay in LR. Pionke et al. (1968) also studied soil properties contributing to LR for a wider selection of soils and produced an expression that includes clay, exchangeable Al, OM, and

change in pH. Gathering data to calculate a LR with such an expression unfortunately does not rate it as a quick-test procedure, and may only be of interest for identifying soil components participating in LR. A LR can generally be more easily obtained using a buffer-pH procedure.

Indirect LR-determination studies suggest that the most important contributing factors to LR are exchangeable Al, OM, and clay contents and the desired change in soil pH. These factors contribute collectively to a LR and cannot be neutralized independently by liming. Accordingly, if liming soils to neutralize potentially toxic levels of Al is envisaged, part of the applied limestone will react with Al but the remainder will neutralize acidity released by other soil components, this neutralization scheme will proceed until soil pH is sufficiently high to complete Al precipitation.

More accurate and complex equations are available for predicting LR for more acid soils than proposed by Keeney and Corey (1963), according to Tran and van Lierop (1981b). As indirect procedures do not offer advantages over buffer-pH procedures, the equation suggested by Keeney and Corey is offered for use when an alternate procedure needing minimal data would be useful. These authors included a typical liming factor (1.6) in their equation. However, its general use may not be justified as suggested in section IV.A. Furthermore, verification by Tran and van Lierop (1981b) suggest the Keeney and Corey equation recommends on the average 130% more limestone than indicated by incubation. The equation is reproduced with its original liming factor.

$$\text{LR (6.5)} = 1.6 (6.5 - \text{soil pH}) \times (\% \text{OM}). \quad [1]$$

2. Comments

The indirect LR estimation procedure proposed by Keeney and Corey (1963) is advanced for use when buffer-pH values are not available and a LR recommendation is required. The procedure is fairly accurate and relies on common soil tests.

VI. LIME REQUIREMENT DETERMINATION OF ACID HISTOSOLS

A. Principles

Acid Histosols are usually limed to a pH around 5.2 to 5.4 (water), which is agronomically comparable to 6.5 for mineral soils (McLean, 1971, 1973, 1982; van Lierop, 1983). A pH of 5.4 (water) corresponds to approximately 5.0 in 0.01 M CaCl₂ (van Lierop, 1981a). Although this pH appears relatively low, crop growth is not affected by excessive acidity. Generally, Histosols contain little extractable Al, and, therefore, probably produce optimum yields at lower pH levels. However, different calibrations are required for determining LR with buffer-pH procedures. Not just because of a differ-

ent target value, but more importantly, because the nature of their exchange complex is different (McLean, 1973, 1982; Mehlich, 1976; van Lierop, 1983; Nõmmik, 1983).

The Mehlich and Nõmmik buffers were originally calibrated for determining the LR of Histosols (Mehlich, 1976; Nõmmik, 1983). However, calibration of the Mehlich buffer was not achieved with incubation reference values, and Nõmmik probably chose pH 7.0 for CEC characterization rather than determining a LR to achieve optimum yields. Unfortunately, liming Histosols to pH 7.0 is too high for optimum crop production and minimizing subsidence (van Lierop, 1981a, 1983).

Although McLean (1973, 1982) published a relationship between the SMP-single buffer soil-buffer pH and LR values to achieve pH 5.2 for organic soils, details of the calibration appear not to have been published. Few buffer-pH verifications have been carried out for Histosols. However, verifications of the single-buffer calibrations were studied by van Lierop (1983). He concluded that the Mehlich-buffer calibration was accurate for determining the LR of acid Histosols. It provides LR values for achieving pH to 5.4 (water). On the other hand, the SMP-single-buffer calibration proposed by McLean (1973, 1982) was found to recommend too high CaCO_3 rates for achieving pH 5.2 (water) for moderate and low requirement soils. Accordingly, improved calibrations and procedural limitations are discussed for the Mehlich, SMP, and Woodruff buffer-pH procedures by van Lierop (1983).

Errors in LR determination for acid Histosols probably have three principal causes: (i) erroneous-assumed bulk density (BD) values, (ii) inaccurate buffer calibration, and (iii) irreversible sample drying. Histosols ought not be dried and weighed for determining LR because the value for a desired plow-layer depth can only be calculated if the bulk density is known. A BD (volume weight) value for Histosols can vary from about 0.1 to 0.7 g mL^{-1} (Kaila, 1956; van Lierop, 1981b). Furthermore, drying increases BD by an average of about 200%; however, field-moist BDs are usually not closely correlated with dried soil values (van Lierop, 1981b; Boelter, 1964). A furrow layer cannot be accurately defined for Histosols without adjusting for differences in BD. Measuring a LR of scooped dried samples will probably not improve accuracy of recommendations, as BD increases with drying, and its modified value is not precisely related to what it was in the original field-moist state. To compound difficulties, dried Histosols are often difficult to rehydrate completely, and CEC properties are likely altered as some drying seems irreversible.

Obviously, LR determination of acid Histosols ought to be made on volumetrically measured field-moist soil samples having a representative field density to improve recommendation accuracy, as inaccuracies are largely related to changes of BD between moist field and dried laboratory samples. The importance of sample BD on LR determination accuracy was recognized by van Lierop (1981b), who proposed a reconstituted BD procedure to simulate original field-moist density in the laboratory. The procedure was used to verify and calibrate the Mehlich (1976), SMP (Shoemaker et al., 1961),

and Woodruff (1948) buffers for determining the LR of acid Histosols. Interestingly, a LR for achieving any other target pH between current soil pH and about 6.0 (water) can be derived from pH 5.4 values as the change in pH is linearly related to amounts of CaCO_3 added.

B. Comments

The SMP, original Woodruff, and Mehlich buffers have similar precision and accuracies for determining the LR of acid Histosols (van Lierop, 1983). Accordingly, it is suggested that if one of these buffers is being used for determining the LR of mineral soils, that it be used with its improved calibration and procedure for organic and Histosols. Buffer-pH LR procedures are about as accurate for acid Histosols as mineral soils. Calibrations are in metric tonnes of CaCO_3 2 million L^{-1} of soil (1 ha to a depth of 20 cm): see section IV.B for information about modifying rates to fit other measurement units.

VII. INDIRECT LIME REQUIREMENT DETERMINATION OF ACID HISTOSOLS

A. Principles

The LR of Histosols containing about 50% or more OM can be determined accurately, and sometimes more conveniently by using the following indirect procedure. It was derived from BD, pH, and incubation-LR data of the Histosols used for calibrating and verifying buffer-pH procedures by van Lierop (1983). The relationship between LR and BD was suggested by the linear changes in pH with increasing additions of CaCO_3 . Slopes of incubation graphs derived by plotting soil pH against additions of CaCO_3 changed with BD. Accordingly, a regression equation was fitted to the relationship between changes in soil pH adjusted to a constant soil BD ($\delta\text{pH} \times \text{BD} = \beta$) and incubation LR values (Fig. 5-2). The relationship implies that a given amount of liming produces the same change in pH with different Histosols when these are adjusted for differences between BD.

$$\text{LR} = 35\beta \quad [2]$$

$$\beta = \delta\text{pH} \times \text{BD} \quad [3]$$

$$r = 0.971^{**}; s_{y.x} = 1.72. \quad [4]$$

The relationship between β and LR values is not very different from that suggested by Keeney and Corey (1963) for determining the LR of mineral soils as they assumed that LR was a function of a desired change in pH (δpH) and soil OM content. The equation estimates the amount of acidity, hence the LR, of acid Histosols. It allows computation of LR for achieving any

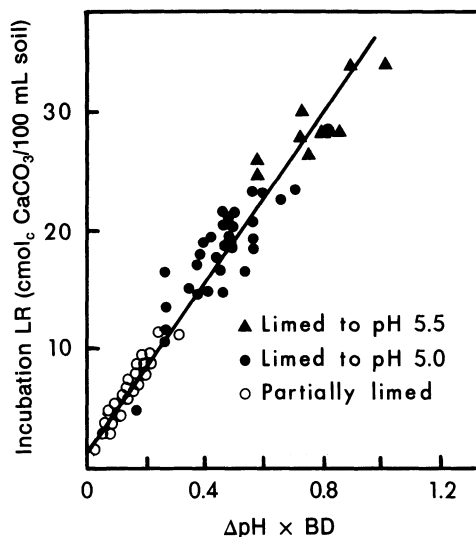


Fig. 5-2. Relationship between LR and β -values ($\Delta\text{pH} \times \text{BD}$) for Histosols in metric tonnes $\text{CaCO}_3 \text{ ha}^{-1}$ (2 million L of soil).

selected target pH between current value up to about 6.0 (water) for soils containing more than about 50% OM. Furthermore, the equation appears to be able to estimate LR when soil pH is determined in 0.01 M CaCl_2 , or when a soil has been partially limed. Calibrations are in metric tonnes of CaCO_3 2 million L^{-1} of soil (1 ha to a depth of 20 cm): see section IV.B for information about modifying rates to fit other measurement units.

B. Procedure

Although no buffer is required to determine LR with this procedure, a soil BD is necessary for calculating the β -value. As field BD is rarely available, the reconstituted BD procedure proposed by van Lierop (1981b) is suggested. Its value is determined by compressing soils into a sturdy (about 17 mL; $\frac{1}{2}$ oz) medicine cup with slightly inclined walls. Actual cup size is not critical but ought to have about the same shape. Soils are compacted into the cup by hand until either no more soil can be pressed in, or water comes to the surface. Thereafter, excess soil is trimmed and the compressed soil transferred to a drying vessel, dried at 105°C , weighed, and the BD is calculated. Subsequently, the β -value is obtained by multiplying BD by the desired change in soil pH (ΔpH). Estimated LR is obtained by multiplying β -value by 35. Lime requirement values should not be expressed with greater precision than one place after the decimal.

C. Comments

This procedure may be convenient for determining LR of acid Histosols when relatively few samples are involved. Although no buffer is necessary,

drying time and space, as well as a balance are required. The procedure has an accuracy similar to a buffer-pH method. Field-moist soil samples, or actual field BD values are required to obtain accurate estimates.

VIII. ALUMINUM AS CRITERION FOR LIMING ACID SOILS

A. Introduction

Aluminum was implicated in the chemistry of acid mineral soils by early research (Jenny, 1961; McLean, 1965). Although Al is abundant in soils, only exchangeable and solution Al occurring at acid pH values have a bearing on LR. Ionic forms in the soil solution are of interest because they are responsible for Al toxicity and poor crop growth on acid soils when present at sufficiently high levels (Ragland & Coleman, 1959; Kamprath, 1970; Evans & Kamprath, 1970; Reeve & Sumner, 1970a, b; Hutchinson & Hunter, 1970; Martini et al., 1974; Hoyt & Nyborg, 1971a; Hoyt & Webber, 1974; Penney et al., 1977; Webber et al., 1982). The amount of Al on the permanent soil-exchange sites is largely influenced by soil pH (Jenny, 1961; McLean, 1976). Aluminum may occupy a large proportion of the permanent exchange sites of highly weathered soils such as Oxisols and Ultisols (Evans & Kamprath, 1970; Reeve & Sumner, 1970a, b). However, the permanent exchange sites are fully saturated with bases other than Al when soil pH is near 5.5 (water) or higher as indicated by extensive lime and corrected lime-potential studies (Clark, 1965, 1966b; Clark & Hill, 1964; Clark & Nichol, 1966; Turner & Nichol, 1962; Turner & Clark, 1965; Singh, 1972). Liming to pH 5.5 ensures elimination of possible Al toxicity, though it will result in liming some soils unnecessarily as they may not contain toxic concentrations of Al (Reeve & Sumner, 1970b). The concentration of exchangeable Al in soils appears to decrease exponentially as soil pH increases (Pionke & Corey, 1967; MacLeod & Jackson, 1967; Thomas, 1967; van Lierop et al., 1982; Nõmmik, 1983).

Soil OM has some influence on the concentration of Al affecting plants as it complexes Al and thus mitigates its toxicity (Schnitzer & Skinner, 1963a, b, 1964; Clark & Nichol, 1966; Evans & Kamprath, 1970). Generally, as soil OM increases, less Al is found in the soil solution at a given pH (Evans & Kamprath, 1970). However, a further mitigating effect of complexed-Al ions on its toxicity to crops was suggested by the work of Foy and Brown (1964) who demonstrated that complexing agents increase the solubility but decrease Al toxicity to Al-sensitive plants. Unfortunately, Al levels that may not affect growth of a crop may be toxic to another, as crops and cultivars have different tolerance to Al toxicity (Foy, 1964; Foy et al., 1965, 1969).

Aluminum is commonly determined using either "flame" (AA or ICAP), colorimetric, or titration procedures (Yuan, 1959; Lin & Coleman, 1960; McLean, 1965; Rich, 1970; Dewan & Rich, 1970; Barnhisel & Bertsch, 1982). However, it should be pointed out that flame procedures include, in addition to extracted ionic-Al, polymerized-Al, and Al-OM complexes since these forms are destroyed, ionized, and detected by flame. Clark (1965) emphasized

the importance of using certain colorimetric means, such as 8-hydroxyquinoline, for determining Al in soil extracts as he found these procedures to reflect ionic-Al concentrations more accurately. Titration and colorimetric procedures seem to have been used more frequently in the cited literature, possibly because exchangeable Al is generally extracted with a concentrated neutral salt that often causes burner salt accumulation with many flame units. Such buildup gradually affects flame intensity and causes signal drift. Consequently, a flame procedure may provide unreliable readings. A buildup requires more frequent equipment cleaning and adjustment. Furthermore, some AA units are less sensitive and precise than titration or colorimetric procedures for determining Al.

Crop yield responses to liming are closely related to exchangeable-Al reductions, though, sensitive plants appear to have some tolerance to low concentrations. Consequently, exchangeable Al does not have to be completely precipitated by liming to enable maximum yield production (Ragland & Coleman, 1959; Hutchinson & Hunter, 1970; Kamprath, 1970; Martini et al., 1974; Reeve & Sumner, 1970b; Hoyt & Webber, 1974; Penney et al., 1977; Webber et al., 1982). A tolerance by crops suggests that convenient determination procedures, like titration or flame, may be employed to determine potentially harmful levels, as a low background—caused by innocuous complexed, polymerized, or low level of exchangeable or ionic forms—would not affect crop productivity.

The main advantage that favors using Al as a liming criterion is that smaller amounts of liming material are required to precipitate plant-toxic Al levels by liming to pH 5.5 than to higher soil pH values. Lower rates have considerable practical benefit where relative costs of liming are high. Many places do not have inexpensive sources for liming agricultural soils, and occasionally, under extensive agricultural production, liming costs may be higher than land costs. Under such circumstances, using Al as liming criterion may result in significant yield improvement and economic advantage. It is often said that liming to a higher pH has potentially beneficial effects on nutrient availability and microbiological activity (McLean, 1970, 1971), and liming to a higher pH does occasionally result in increased yields. However, liming a very acid soil at high levels can also decrease yields by inducing plant nutrient deficiencies. As it is not the objective of this section to clarify these schools of thought, suffice perhaps to say that if liming costs are low, slowly liming an acid soil to a pH around 6.0 will not adversely affect yields. However, where liming costs are high using Al, or Al and pH levels to decide whether liming is required has advantages. Generally, maximum yields are attained when plant-toxic levels of Al are eliminated and plant nutrients are in adequate supply. Liming at these low levels, however, may require more frequent additions to maintain soil pH.

B. Approaches and Procedures

1. Neutralization of Possible Aluminum by Liming to pH 5.5

a. Principles. Probably the simplest approach when using Al as liming criterion is to assume that soils that have a pH < 5.5 contain potentially

toxic levels. Liming these soils to a $\text{pH} \geq 5.5$ neutralizes it and enables obtaining maximum crop yields when plant nutrient supplies are adequate. This approach relies on measuring LR to $\text{pH} 5.5$ with a buffer- pH procedure, and subsequently liming the soil. The original calibration of the Mehlich buffer- pH procedure (Mehlich, 1976) was developed to neutralize acidity harmful to crop growth which includes potentially toxic levels of Al. Consequently, it or another proposed buffer- pH procedure can be used to ensure optimal yields at relatively low-liming costs. However, some mineral soils with a pH between 4.9 and 5.5 (water) do not contain crop-toxic levels of Al, these would be limed without producing increased yields. Liming these soils, however, may increase pH , improve cropping opportunities, and delay further acidification.

C. Liming to $\text{pH} 5.5$ when Exchangeable Aluminum is High

1. Principles

This approach is more onerous as an additional test is required to determine whether soils with pH values between 4.9 and 5.5 contain sufficiently high levels of Al to be plant-toxic and hinder growth. It averts liming soils that might not respond to liming with increased yields. Soils with $\text{pH} \leq 5.5$ and containing higher-exchangeable-Al levels than a selected norm are tested for LR to $\text{pH} 5.5$ using a buffer- pH procedure, and subsequently limed.

Moschler et al. (1960) obtained maximum alfalfa yields when exchangeable-Al levels were below $0.2 \text{ cmol}_c \text{ Al kg}^{-1}$ of soil. Ragland and Coleman (1959) reported good sorghum [*Sorghum bicolor* (L.) Moench] growth when limed soils contained $\leq 0.1 \text{ cmol}_c$ exchangeable Al kg^{-1} . However, oat, alsike clover, and grass yields were not increased by liming soils that initially contained about $1 \text{ cmol}_c \text{ Al kg}^{-1}$. Reeve and Sumner (1970a, b) proposed using an exchangeable-Al index (EAI) and suggested that sorghum yields were not increased by liming, if soils contained $< 0.2 \text{ cmol}_c \text{ Al kg}^{-1}$ soil. Hoyt and Nyborg (1971a, 1987) found the concentration of exchangeable Al in soils to be a good indicator for predicting response to liming. Furthermore, data of Hoyt and Webber (1974) and Webber et al. (1982) indicates that maximum barley yields were obtained when exchangeable-Al concentrations were $0.2 \text{ cmol}_c \text{ kg}^{-1}$ or lower.

Survey of the above studies suggests that maximum yield of relatively Al-sensitive crops like alfalfa, soybean, and barley is realized when the exchangeable-Al level is lower than $0.1 \text{ cmol}_c \text{ Al kg}^{-1}$ of soil. Accordingly, this level was selected as the testing norm. Crops more tolerant to Al can be grown successfully at this or higher Al concentrations. Soils that have a $\text{pH} \leq 5.5$ and contain more 1 N KCl or $0.2 \text{ N NH}_4\text{Cl}$ extracted Al than $0.1 \text{ cmol}_c \text{ kg}^{-1}$ of soil (about $10 \mu\text{g}$ of Al g^{-1} or mL^{-1} of soil) are limed. Lower Al levels are found in soils with a pH between 4.9 and 5.5 (Clark, 1965, 1966b; Clark & Hill, 1964; Clark & Nichol, 1966; Turner & Nichol, 1962; Turner & Clark, 1965; Singh, 1972; Hoyt & Webber, 1974; Penny et al., 1977; Webber et al., 1982). However, using this approach, soils containing lower Al levels need not be limed or tested for LR.

2. Equipment

1. Buchner funnels and appropriate Whatman no. 42 or equivalent filters.
2. Mechanical shaker.
3. Automatic pipette.
4. 2.5-mL scoop soil measure.

3. Reagents

Either 1 *N* KCl: dissolve 74.56 g of KCl (FW = 74.56) per liter.

Or 0.2 *N* NH₄Cl: dissolve 10.5 g of NH₄Cl (FW = 53.49) per liter.

4. Procedures

1 *N* KCl exchangeable Al: Measure 2.5 mL⁴ dried and sieved (≤ 2 mm) soils with pH between 4.9 and 5.5 into Erlenmeyer flasks. Add 25 mL of 1 *N* KCl and shake 30 min at about 180 cycles per minute. Filter with gentle suction. Determine Al by one of the procedures described by McLean (1965) or Barnhisel and Bertsch (1982).

0.2 *N* NH₄Cl Extracted Al: This procedure relies on the EAI proposed by Reeve and Sumner (1970a). Measure 2.5 mL⁴ dried and sieved (≤ 2 mm) soils with pH between 4.9 and 5.5 into Erlenmeyer flasks. Add 25 mL of 0.2 *N* NH₄Cl and shake for 2 min at about 180 cycles min⁻¹. Filter with gentle suction. Determine Al by one of the procedures described by McLean (1965) or Barnhisel and Bertsch (1982).

5. Comments

Soils with pH values between about 4.9 and 5.5 and containing ≥ 0.1 cmol_c Al L⁻¹ extracted with 1 *N* KCl or 0.2 *N* NH₄Cl are tested for LR with a buffer-pH procedure and limed to pH 5.5. Soils with pH < 4.9 are tested for LR and limed to pH 5.5.

D. Liming to pH 5.5 when Soil-Solution Aluminum is High

1. Principles

This approach is similar to section VIII.C except that *soil-solution* is substituted for *exchangeable* Al as additional test criterion. Soils with pH values between 4.9 and 5.5 are tested for soil-solution (soluble) Al to select those that contain plant-toxic levels. The additional test allows choosing soils that might respond to liming with increased yields. Soluble Al is extracted with a dilute neutral salt solution as 0.01 *M* CaCl₂. Soils containing higher concentrations of soluble Al than the selected norm are tested for LR using a buffer-pH procedure, and subsequently limed to achieve pH 5.5.

Although it is difficult to determine from the literature whether improved liming response recognition is obtained with *soluble* instead of *exchangeable* Al as the screening norm, as researched soils were probably not randomly

selected. Perusal of published data suggest, nonetheless, that a proportion of soils limed by using the 0.1 cmol_c exchangeable-Al criterion, would not be, had a 1 μ g (0.01 *M* CaCl₂) soluble Al norm been used instead. A further advantage favoring 0.01 *M* CaCl₂, is that it does not cause burner salt-buildup problems with flame techniques.

Extracting 0.01 *M* CaCl₂ soluble Al is realized at the same soil/solution ratio and concentration as for determining soil pH; accordingly both tests can be carried out on the same sample by filtering pH samples and determining Al in the extracts. Particularly, since Al concentrations extracted by 0.01 *M* CaCl₂ are not extraction-time sensitive (Hoyt & Webber, 1974). However, instead of using soil pH values ranging between 4.9 to 5.5 (water) as selection parameters for determining soluble Al, corresponding 0.01 *M* CaCl₂ pH situated between about 4.4 and 5.0 should be used instead.

Interest in soluble Al as screening norm evolved because exchangeable Al is not always a good indicator for determining crop response to liming (Ragland & Coleman, 1959; Adams & Lund, 1966; Kamprath, 1970; Evans & Kamprath, 1970; Martini et al., 1974; Webber et al., 1982). There are several possible reasons for this. First, plants have some tolerance to Al; therefore, levels need not be brought to zero. Second, high levels of exchangeable Al do not necessarily translate into high soil-solution levels that can affect plant growth (Evans & Kamprath, 1970). Milder extraction solutions such as 0.01 *M* CaCl₂ were proposed to measure potentially toxic concentrations of soluble Al (Hoyt & Nyborg, 1971a; Webber et al., 1982). Thirdly, Al impairs Ca and Mg absorption, and high levels of the latter seem to counteract its toxic effect. This was the reason that percentage Al saturation was suggested as an index for predicting yield response to liming (Adams & Pearson, 1967; Kamprath, 1970; Evans & Kamprath, 1970; Martini et al., 1974; Webber et al., 1982). However, obtaining a percentage Al or base saturation is more laborious, proposed values vary widely, and serve only to emphasize that exchangeable Al does not generally need to be completely neutralized to achieve maximum crop yields (Adams & Pearson, 1967; Kamprath, 1970; Evans & Kamprath, 1970; Martini et al., 1974; Penney et al., 1977; Webber et al., 1982).

Soil-solution Al concentration was determined in 0.01 *M* CaCl₂ for corrected lime-potential studies (Clark, 1965, 1966b; Clark & Hill, 1964; Clark & Nichol, 1966; Turner & Nichol, 1962; Turner & Clark, 1965; Singh, 1972). Soluble Al is the principal toxic substance in acid soils (Ragland & Coleman, 1961; Hourigan et al., 1961; Kamprath, 1970; Reeve & Sumner, 1970a, b), and soil-solution Al is an index of its potential toxicity. Accordingly, Hoyt and Nyborg (1971a, b) proposed using 0.01 *M* CaCl₂ at a 1:2 soil/solution ratio as a diagnostic test for determining potentially toxic concentrations of Al and Mn in acid soils. Subsequently, the procedure was refined by demonstrating that Al values obtained with Clark's 5-d procedure (Clark, 1965) and 16- and 1-h extraction times variations provided equally good correlations between Al and crop yield data (Hoyt & Nyborg, 1971a, 1972). The extraction time was shortened further from 1 h to 5 min as the procedure is not time sensitive (Hoyt & Webber, 1974). Doubling extracting solution

concentration from 0.01 to 0.02 M CaCl_2 gave equally good correlations between Al and crop data (Hoyt & Nyborg, 1972; Hoyt & Webber, 1974). The more concentrated 0.02 M CaCl_2 solution is suggested because it removes about twice as much Al and may provide better analytical precision (Hoyt & Nyborg, 1972; Hoyt & Webber, 1974; Webber et al., 1977; Hoyt & Nyborg, 1987). However, a 0.01 M CaCl_2 solution has been used as effectively over the years (Hoyt & Nyborg, 1971a, 1972; Hoyt & Webber, 1974; Webber et al., 1977, 1982), and has the advantage of being more versatile as it can be used to measure soil pH and extract soluble Al from the same sample. It was selected, therefore, for diagnosing soluble Al levels in acid soils.

Unfortunately, neither proponents of exchangeable or soil-solution Al have proposed a test norm vociferously for deciding whether Al concentrations are sufficiently high to affect yields. However, a standard was used (1 μg of Al mL^{-1} soil extracted with 0.02 M CaCl_2) when verifying LR-determination procedures by Webber et al. (1977). Study of published data suggest that yields are not affected by excessive acidity when soluble Al levels in 0.01 M CaCl_2 are lower than about 1 μg of Al mL^{-1} soil (Hoyt & Nyborg, 1971a, 1972; Hoyt & Webber, 1974; Webber et al., 1982). Utilization of this norm does not imply that maximum yields cannot be attained at higher Al levels in some soils. The norm is meant for determining whether a soil-solution Al level is low enough not to affect yield of sensitive crops. Validity of the 1 μg of Al mL^{-1} soil (0.01 M CaCl_2) test norm for accomplishing this objective was confirmed by P.B. Hoyt (1988, personal communication). Furthermore, comparison of corresponding soluble or 0.1 cmol_c exchangeable-Al norms to yield data revealed that the 1 μg of soluble Al mL^{-1} soil test criterion is applicable to a wide range of soils.

2. Equipment: See section VIII.C.2.

3. Reagents: See section III.D.1.

4. Procedure

Measure 10 mL^5 of dried and sieved (≤ 2 mm) soils with pH between about 4.4 and 5.0 (0.01 M CaCl_2) or between 4.9 and 5.5 (water) into Erlenmeyer flasks. Add 20 mL 0.01 M CaCl_2 and shake 5 min at about 180 cycles min^{-1} . Filter using gentle suction. Determine Al by atomic absorption (Webber, 1974; Webber et al., 1982), or by a procedure described by McLean (1965) or Barnhisel and Bertsch (1982).

5. Comments

Soils with pH values between about 4.5 and 5.0 (0.01 M CaCl_2) or about 4.9 and 5.5 (water) containing more than about 1 μg of soluble Al mL^{-1} soil are tested for LR with a buffer-pH procedure and limed to pH 5.5. Soils with lower pH values are tested for LR and limed to pH 5.5.

E. Calculating Lime Requirement Rates from Exchangeable-Aluminum Levels

1. Principles

The effect of exchangeable Al on crop yield was introduced in section VIII.C.1. It was proposed then that exchangeable Al be used as additional test criterion to determine whether levels were high to warrant liming. If they were high then a buffer-pH test would be used to determine LR, and the soil limed to pH 5.5. In this section, an alternative approach that relies on calculating LR levels from the concentration of exchangeable Al is proposed. Using this approach, exchangeable Al is determined on soils with $\text{pH} \leq 5.5$.

Exchangeable-Al levels as high as 30 and 26 $\text{cmol}_c \text{ Al kg}^{-1}$ soil have been reported by Ragland and Coleman (1959) and Mengel and Kamprath (1978), respectively. However, most values are situated between 0 and 4 $\text{cmol}_c \text{ kg}^{-1}$ soil. The advantage in using exchangeable Al for deriving LR is that liming rates expand as Al levels and toxicity increase. Accordingly, soils containing high or no exchangeable Al will be limed at corresponding rates. Nonetheless, the fundamental reason for interest in this approach is that rates so derived are usually much lower than required for reducing soluble Al to nontoxic levels or increasing soil pH to 5.5. For example, a soil containing 3 cmol_c exchangeable Al would require liming at an equivalent 3 t $\text{CaCO}_3 \text{ ha}^{-1}$ to grow relatively Al-tolerant crops. While this example conveys the principle of the exchangeable-Al approach, a liming factor is often included in LR rates to increase these and thereby enable growing more Al-sensitive crops. Data supplied by Webber et al. (1977) suggests that an average of about one-fifth the limestone required to achieve pH 5.5 would be applied using exchangeable Al. Their data also shows that an average of one-third the limestone required to reduce soluble-Al to nontoxic levels would be applied using rates based on exchangeable Al without liming factor.

At pH values below 5.5 (water) most of the soil-buffering capacity is related to exchangeable Al (Jackson, 1963; Kamprath, 1970; Reeve & Sumner, 1970a, b), and others. Consequently, liming at rates equivalent to the concentration of exchangeable Al react primarily with Al as shown by Kamprath (1970). He proposed using exchangeable-Al levels for calculating liming rates by multiplying values by either 1.5 or 2.0 for very Al-sensitive crops. Kamprath's work, Ragland and Coleman (1950), and Evans and Kamprath (1970) support the premise that such rates are ample for obtaining maximum yields. Although this liming scheme appears valid for determining rates for heavily leached soils, such as those used in these studies, it is not clear how widely applicable this approach is for liming different soils. Section V.A discusses the contribution of various soil properties in regulating LR. In any event, data from Webber et al. (1977) suggest that rates based on exchangeable Al, as proposed by Kamprath (1970), can be high enough to achieve pH of 5.5 or higher and therefore maximum yields. However, using this liming scheme will result in liming insufficiently for neutralizing Al in some soils. Still, Al need not be completely precipitated for achieving maximum yields

for most crops. This liming scheme appears to offer the possibility of achieving maximum yields for many crops with the lowest liming rates. Of course, if liming costs are relatively low, using this approach offers little or no advantage. However, for extensive agricultural production where liming is a relatively important production cost, as it is in many parts of the world, using exchangeable Al for determining rates offers a reasonable alternative approach for maintaining or improving production and soil quality.

2. Equipment: Same as described in section VIII.C.2.

3. Reagent: Prepare 1 N KCl as described in section VIII.C.3.

4. Procedure

Extract 1 N KCl exchangeable Al as described in section VIII.C.4. Liming rates are calculated using the following equations suggested by Kamprath (1970) and discussed by McLean (1982).

$$\text{LR(I)} = \text{Al} \quad [5]$$

$$\text{LR(II)} = 1.5\text{Al} \quad [6]$$

$$\text{LR(III)} = 2\text{Al} \quad [7]$$

where LR(I), LR(II), and LR(III) represent the LR in metric tonnes of $\text{CaCO}_3 \text{ ha}^{-1}$ (2 million L) for crops having most, moderate, and least Al tolerance, respectively. The Al concentrations in these equations are expressed in $\text{cmol}_c \text{ Al L}^{-1}$ of soil. Aluminum is considered trivalent and fully ionized. These assumptions generally result in liming at higher rates than if true ionic Al concentration were considered.

5. Comments

This LR-determination approach has particular applicability where large tracts of land suitable for extensive agricultural production are being under utilized because of excessive acidity and high-liming costs. Liming rates based on Al as a criterion will enhance productivity at the lowest possible cost and slow the rate of soil acidification. This liming approach will provide optimal yields in many situations and is a step in the right direction for others.

IX. LIMING RECOMMENDATIONS AND LIMING

A LR is the amount of CaCO_3 required by a hectare furrow-layer of soil to neutralize acidity and increase pH to a selected target value or neutralize exchangeable Al. To effect neutralization efficiently and accurately, the liming rate has to be incorporated uniformly into a furrow-layer, which is often assumed to have a depth of 20 cm ($2 \text{ million L ha}^{-1}$; van Lierop,

1989). To achieve that end, the liming material must first be spread precisely and uniformly over the soil surface, and subsequently mixed thoroughly into the furrow layer. Generally, it is difficult to satisfy these requirements with a single application or incorporation. However, certain management practices favor attaining the desired end as efficiently as possible. One of these is to adjust the liming rate to fit tillage depth. For example, if applied limestone is only worked into 10 cm (4 in.) soil, the recommended rate should be reduced by one-half because only one-half the assumed furrow layer is being limed. On the other hand, if limestone is left on the soil surface to gradually find its way down, the rate can best be reduced to a minimum application, followed by others as it moves down the profile. Limestone so applied will gradually neutralize acidity at depth by moving through the profile at an approximate rate of 1 to 2 cm y^{-1} where moisture and drainage are adequate (Brown et al., 1956). Not adjusting liming rates for differences between assumed and actual furrow-layer depths may cause localized overliming, particularly if rates and target values are high. The only advantage to liming to a higher pH than required for achieving maximum yields is that a longer period may lapse before liming is required again for maintaining soil pH.

The principal liming inaccuracies are caused by uneven spreading and incorporation. Generally, spreading uniformity is improved by applying a LR in two or more increments. Similarly, incorporation uniformity is improved by increasing the intensity and number of tillings. For example, a more accurate liming will result if a LR of 15 t is applied in three separate additions of 5 t of limestone ha^{-1} . Whether a LR is applied in several increments or as a single application depends of course on the size of the initial LR rate. Perhaps a single application should ≥ 5 to 6 t ha^{-1} . Incremental liming need not cost more, but may require more than one growing season to complete. However, using fewer amendment additions is justified when soils are tilled infrequently at depth: taking advantage of such an opportunity may be advantageous. It is well to remember when partially liming a furrow layer, that the greatest impact on yields results if liming is restricted to the upper portion of the soil (Hourigan et al., 1961; Lathwell & Peech, 1965). The applied liming material will gradually move down and neutralize acidity at depth while the upper soil layer is relimed to maintain pH (Brown et al., 1956).

Portioning a LR into several increments will enhance its distribution through the profile and assist in maintaining surface pH (Brown et al., 1956). Principally, because large LRs ought to be applied in multiple increments, the calibration accuracy of buffer-pH procedure is less important for soils with high requirements. Presumably, those soils will be tested again before a last corrective LR increment is broadcast to monitor pH progress and decide on future management. On the other hand, highly accurate buffer-pH calibrations are required to determine the LR of soils with low-buffering capacities as they will usually be limed with a single application. Accuracy of determination and application is, therefore, particularly important at low rates.

Limestone can neutralize soil acidity quite rapidly. In fact, soil pH can be increased by several units in a matter of minutes when liming a very acid soil, though a stable pH will not result for some time. Generally, most of the change in pH occurs shortly after liming. Subsequently, it continues to increase more gradually and eventually plateaus. Thereafter, it remains there for a period, to finally slowly decline (fluctuating during the course of this generalized cycle). Field studies suggest that soil pH usually peaks within 8 to 12 wk after liming. However, it appears more difficult to increase the pH of a soil with a relatively high than low value. For example, increasing the pH from pH 6.5 to 7.0 is more difficult than from pH 5 to 6.5. Limestone reactivity probably decreases because liming has lowered the intensity of acidity present, as indicated by an increased pH. Occasionally, a soil is limed with dolomitic limestone to correct a low-available Mg level, as this may be the least-expensive source for that nutrient. Liming with dolomitic limestone offers some advantages when soil Mg levels are low, and can be as effective as calcitic limestone for correcting pH. Whether it is used is largely a matter of relative cost.

Measured LR_s are often adjusted by multiplying CaCO₃-LR values by a constant, between 1.4 and 1.5, referred to as a liming factor (Shoemaker et al., 1961; Woodruff, 1948; Adams & Evans, 1962; McLean, 1973, 1982). It is used partially to correct for the inability to achieve a homogeneous dispersion of liming material through a furrow layer, and partially because larger particles in commercial limestone dissolve more slowly. At the risk of breaking with established practice, it is difficult to justify using a typical liming factor blindly, as commercial limestones often have agricultural values (AV) (Murphy & Follett, 1978) that are not significantly different from 100%. The AV of available limestones probably ought to be known so that the better grades can be selected. In any event, correcting LR recommendations by using an arbitrary AV does not seem to offer advantages, particularly if liming is carried out in multiple applications as recommended.

Several procedures have been suggested to evaluate the efficacy of limestone for neutralizing soil acidity (Barber, 1984). Efficacy of a liming material is affected by its solubility. However, more importantly its solubility is largely related to surface area exposed to chemical reaction. This area increases in inverse proportion to particle fineness (i.e., halving the particle size doubles the surface area). A practical approach for evaluating agricultural limestones is achieved by rating sieve fractions and summing their effect. Such a rating procedure compensates for differences in overall fineness. Although, sieves and ratings vary somewhat from one procedure to another, the Ohio and Canadian methods described by Tisdale and Nelson (1966) and Tisdale et al. (1985), or the procedure proposed by Murphy and Follett (1978) are fairly typical. Admittedly, the accuracy of LR recommendations may be improved by adjusting the rate for the agricultural value of the particular liming produce used, as proposed by Murphy and Follett (1978). Probably such adjustments would only improve the accuracy of liming if a limestone had an AV that is significantly lower than about 90%. However, values are rarely known for a specific limestone, even less for a specific lot. Accordingly, using

a customary liming factor does little to improve liming accuracy. Its only material contribution to accuracy is to increase recommended rates proportionately (about 50%).

Hydrated lime is occasionally substituted for limestone; however, a recommended LR should then be reduced by 26% (multiply LR by 0.74). Hydrated lime costs more, and is occasionally used because it is believed to neutralize soil acidity and increase pH more rapidly than limestone. If the effect is to be more rapid, it should be incorporated into the furrow layer as soon after application as possible. If left on the soil surface for any length of time, it will quickly absorb CO_2 from the air to become CaCO_3 . Although, hydrated lime can neutralize soil acidity more rapidly under some circumstances, generally it is not more efficient than a limestone having the equivalent particle-size distribution. However, hydrated lime is often more finely pulverized than limestone and may, therefore, act more quickly.

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Chapter 6

Testing Soils for Available Nitrogen¹

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Crops are probably more often deficient in N than in any other element and yet there are no widely accepted methods of testing soils for this nutrient other than testing for residual nitrate-nitrogen ($\text{NO}_3\text{-N}$) and ammonium-nitrogen ($\text{NH}_4\text{-N}$). This is largely because 97 to 99% of the N in the soil is present in complex organic compounds and slowly becomes available to plants through microbial decomposition. The problems of developing a test for available N are that: (i) The rate at which microorganisms decompose soil organic matter (OM) is dependent on temperature, moisture, aeration, type of organic matter, pH and other factors and (ii) the inorganic forms of N produced are subject to leaching, fixation, denitrification, and other losses. Thus, it becomes difficult to predict either when N will become available, how much will become available or what will happen to it.

The broad spectrum of conditions affecting availability of N to growing crops may be identified at one extreme by cold-humid environments. Under these conditions, soil OM content is high and mineralization of organic N supplies a significant portion of the total requirement for the short-season crops typical of this environment. In these situations, soil OM could be expected to provide a suitable N availability index. Hot, dry environments, typical of the southwestern USA, represent the other extreme. Under these conditions, cultivated crops are almost always irrigated and high yielding. Soil OM levels are very low ($< 1.0\%$) and mineralizable N provides only a small portion of the total N required for high-yielding crops. In these situations, a test of soil $\text{NO}_3\text{-N}$ is a good direct measure of available N. Between these extremes there is a myriad of conditions under which available soil N may be identified by combinations of indirect and direct measures. In some cases, even the best application of existing tests may provide only a poor measure of available N.

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Because of the importance of N in crop production, many agronomists and soil scientists have worked on soil test methods for N. Research on this subject has been reviewed by Harmsen and Van Schreven (1955), Bremner (1965a), Harmsen and Kolenbrander (1965), Dahnke and Vasey (1973), Keeney (1982), and Stanford (1982). Most of the studies discussed in these reviews were concerned with developing procedures to predict the amount of N that will become available during the growing season by mineralization of OM.

The following will briefly discuss that topic but will also discuss some of the testing methods for residual inorganic N and how the test results are used to aid growers in N fertilization.

I. NITROGEN-AVAILABILITY INDEXES

Nitrogen-availability tests can be either biological or chemical. Biological tests are considered by many to be the most reliable because living organisms are used, but they have the disadvantage of usually taking much more time to conduct than chemical tests.

Nitrogen-availability indexes are a measure of the potential of a soil to supply N to plants when conditions are ideal for mineralization. They do not include existing inorganic N present when the soil was sampled. Surface soils usually contain between 0.08 and 0.4% total N, mostly in the organic form (Bremner, 1965b; Stevenson, 1982). The amount that mineralizes each year is commonly in the range of 1 to 3% (Broadbent, 1984) but depends on the amount and type of recent plant residue and environmental conditions. One reason it has been difficult to correlate these tests with plant growth is that the rate at which mineralization of N takes place under field conditions is controlled by several unpredictable environmental factors such as temperature, moisture, and aeration. In spite of this, there are many instances in which favorable results were obtained using N-availability tests (Allison & Sterling, 1949; Fitts et al., 1953; Hanway & Dumenil, 1955; Munson & Stanford, 1955; Cook et al., 1957; Kresge & Merkle, 1957; Saunders et al., 1957; Eagle & Matthews, 1958; Olson et al., 1960; Eagle, 1961; Clement & Williams, 1962; Gasser & Williams, 1963; Eagle, 1963; MacLean, 1964; Keeney & Bremner, 1966a; Robinson, 1968; Stanford & Legg, 1968; Stanford & Smith, 1976; Shumway & Atkinson, 1978; Fox & Piekielek, 1978; Powers, 1980; Saito & Ishii, 1987).

The data indicate that long-term biological indexes (Stanford & Smith, 1972) will give more useful results than short-term biological indexes. This is because short-term incubation tests are influenced to a greater extent by sample pretreatment (Stanford et al., 1974). Preincubation conditions that influence the results of incubation tests were reviewed by Bremner (1965a). He pointed out that incubation results for mineralizable-N in soils are influenced by method of sampling, drying, grinding, sieving, storing, and incubating. The biological N index recommended by Keeney (1982) is that of Waring and Bremner (1964) which determines the amount of $\text{NH}_4\text{-N}$

produced under waterlogged conditions. The soil sample is incubated at 40 °C for 7 d, and the amount of $\text{NH}_4\text{-N}$ formed is determined. The amount of $\text{NH}_4\text{-N}$ in the soil before incubation is also determined. Mineralizable N is calculated as the difference between the results of these analyses.

Most of the N being mineralized in soil obviously comes from a fraction of the soil organic matter that is easily decomposed. Therefore, it is likely that a mild acid or alkaline extractant could make a suitable chemical extractant (Henkinson, 1968; MacLean, 1964; Keeney & Bremner, 1966b; Stanford & DeMar, 1970). A chemical availability index could have the advantage of being simple or rapid. Keeney (1982) recommends the procedure of Stanford and DeMar (1969) as modified by Smith and Stanford (1971) and Stanford and Smith (1976). This procedure involves the determination of $\text{NH}_4\text{-N}$ formed when a soil sample is autoclaved for 16 h at 121 °C.

A procedure that is currently being used in Europe (Nemeth, 1979) is electro-ultrafiltration (EUF). This procedure is an adaptation of the electrodialysis technique described by Mattson (1926). The basic difference is that EUF uses a polycarbonate micropore filter as a membrane and suction to remove the secondary products of electrodialysis. The removal of these secondary products from the soil solution minimizes the effect of electrodialysis on soil pH. This procedure measures $\text{NO}_3\text{-N}$ as well as other forms of N.

Trials on 4000 farms in Austria showed a close correlation between EUF-N values of soil samples taken in June and July and sugarbeet (*Beta vulgaris* L.) yield and quality the following year (Nemeth, 1979). It was found that 1 mg of EUF extractable N per 100 g of soil extracted at 20 °C and 200 V was equal to 30 kg of fertilizer N ha^{-1} (Wiklicky, 1982).

II. RESIDUAL INORGANIC NITROGEN

The potential of a soil to mineralize N compounds as measured by N availability indexes, should be fairly constant from year to year unless the type of crop or amount of crop residue changed. The amount of residual $\text{NO}_3\text{-N}$ will be influenced by these and many other factors. Therefore, it is necessary to test for residual $\text{NO}_3\text{-N}$ each year. Residual inorganic N soil tests are most appropriate shortly before planting to early in the growing season (Stanford, 1982).

For many years, the amount of $\text{NO}_3\text{-N}$ in the soil was ignored or dismissed in the scientific literature as not being important because it is variable or low in concentration (20 kg ha^{-1} or less). For these reasons, Harmsen and van Schreven (1955) and Bremner (1965) thought that a measure of initial N was of little or no value. In recent years, the inorganic N content of the rooting zone (instead of only the 0–15 cm depth) has been reexamined following the example of early workers such as King and Whitson (1901, 1902). In the following sections, the use of the initial inorganic N tests in predicting crop response to N will be discussed.

A. Nitrate-Nitrogen

While the use of the residual $\text{NO}_3\text{-N}$ test has become well established in western Canada (Soper & Huang, 1963) and the Great Plains of the USA (Leggett, 1959; Young et al., 1967; Carson, 1975; Geist et al., 1970; Herron et al., 1977) in the last 20 yr, a test for $\text{NO}_3\text{-N}$ was first proposed in the early 1900s (King & Whitson, 1901, 1902; King, 1905; Buckman, 1910; Call, 1914).

The study of $\text{NO}_3\text{-N}$ is complicated by the fact that: (i) this form of N can move up or down in the soil profile in response to drying and wetting conditions; (ii) $\text{NO}_3\text{-N}$ can be rapidly immobilized by soil microorganisms if a suitable source of energy is present, only to reappear after a short time as the microorganisms reduce the C/N ratio of the energy source (Harmsen & Kolenbrander, 1965); and (iii) up to 70% of applied fertilizer N can be lost by denitrification (Firestone, 1982). In spite of these difficulties, numerous studies since 1950 (Dahnke & Vasey, 1973; Carter et al., 1974; Carson, 1975; Magdoff et al., 1984; Gelderman et al., 1988) have shown that tests for residual $\text{NO}_3\text{-N}$ are helpful in determining N fertilizer needs of crops. A residual $\text{NO}_3\text{-N}$ test is especially useful for short-season, fast growing crops that do not allow much time for mineralization to take place. It is also especially useful when the amount of residual $\text{NO}_3\text{-N}$ in the soil is high at planting time. In this situation, it would not be beneficial to add fertilizer N. However, when the soil is low in residual $\text{NO}_3\text{-N}$, the amount to apply cannot be accurately predicted. Thus, there is a need for an N-availability index to improve N fertilization.

B. Ammonium Nitrogen

Many environmental factors, such as aeration, temperature, moisture content, pH and soil nutrient content affect the production of ammonium nitrogen ($\text{NH}_4\text{-N}$) from OM. Many investigators agree that reduced aeration, as in high moisture soils, high temperatures, and low pH all favor ammonification over nitrification (Harmsen & Kolenbrander, 1965). Thus, when conditions are less favorable for plant growth it is more common to find an accumulation of $\text{NH}_4\text{-N}$ in the soil. Under favorable growing conditions, $\text{NH}_4\text{-N}$ levels are usually quite low except for variable periods after the application of an NH_4 fertilizer. Not many soil testing programs include $\text{NH}_4\text{-N}$ in testing for residual inorganic N.

C. Soil Sampling for Residual Inorganic Nitrogen

The number of soil samples that need to be taken per field, depth of profile samples, time of sampling, and how the samples are handled are all important factors in a successful soil testing program.

The number of subsamples that should be taken to represent a field for residual $\text{NO}_3\text{-N}$ testing depends on the accuracy and precision desired. A study by Swenson et al. (1984) indicated it is necessary to take approximately 20 subsamples per field in North Dakota to obtain an accuracy of $\pm 15\%$

for $\text{NO}_3\text{-N}$ at a precision level of 80%. The number of subsamples needed for that accuracy and precision varied little as field size increased from 10 to 40 ha. This reflects the fact that the level of $\text{NO}_3\text{-N}$ varies as much over relatively short distances as it does over long distances in a particular field. To accurately map soil fertility would probably require sampling fields on a grid of <30 m.

The profile depth to sample for residual $\text{NO}_3\text{-N}$ depends on climate, soil, and crop to be grown. Samples are usually taken to a depth of 60 cm (Smith, 1977) but many studies have found that the correlation between residual $\text{NO}_3\text{-N}$ and crop yield increases as depth of sampling increases within the rooting depth. More humid climates may require deeper sampling. The soil type will influence depth of rooting and water movement.

The time to sample depends on climate. In relatively cold and dry areas, such as the Northern Great Plains, soils can be sampled for residual $\text{NO}_3\text{-N}$ from early fall to planting the following spring (Dahnke & Vasey, 1973). In more humid areas, the best sampling time may be after the crop has started to grow (Magdoff et al., 1984).

Shortly after a soil sample is taken, it should be treated to stop mineralization. It is especially important to do this when the soil is sampled in late fall or winter in temperate climates. If cold ($<10^\circ\text{C}$) soil is brought into a warm building for any amount of time, the sample will no longer represent the status in the field. Mineralization will take place in the sample but will not be taking place in the field. The most common and practical way to stop mineralization is to air dry the sample by spreading it out in a thin layer. Other methods that have been used are freezing or the addition of a biological inhibitor, such as toluene (Bremner, 1965; Storrier, 1966). These latter methods are inconvenient or ineffective.

III. METHODS OF DETERMINING RESIDUAL NITROGEN

There are many methods for the determination of NH_4 , nitrite (NO_2) and $\text{NO}_3\text{-N}$ in soils. The advantages and disadvantages of some of these methods were discussed by Keeney and Nelson (1982).

Details of the procedures listed in Table 6-1 are given in the paper by Keeney and Nelson (1982).

An additional procedure not discussed in their paper is ion chromatography (Dick & Tabatabai, 1979; Nieto & Frankenberger, 1985). This method is rapid, sensitive, and precise. It can be used to simultaneously detect chloride, NO_2 , NO_3 , and sulfate (SO_4). The time and sensitivity will be largely determined by the type and length of the ion exchange column.

IV. CROP NITROGEN REQUIREMENT

Knowledge of the amount of N removed by a crop is necessary for the interpretation of a N soil test (Johnson, 1982). Crop N removal is obtained by multiplying the concentration of N in the crop by the crop yield. Crop

Table 6-1. Methods for the determination of inorganic forms of N in soil extracts. (After Keeney & Nelson, 1982.)

Method of analysis	Concentration range in extract mg L ⁻¹	Interferences	Comments
		<u>NH₄-N</u>	
Indophenol blue	0.005-20	Calcium and Mg	Simple and rapid
Ion electrode	0.1-1400	Volatile amides	Sensitive, rapid
Steam distillation with MgO	0.1-1000	Volatile amides	Rapid, widely used
Microdiffusion with MgO	0.1-100	None	Simple
		<u>NO₂-N</u>	
Griess-Ilosvay	0.1-12	None	Sensitive
Steam distillation with Devarda alloy after NH ₂ SO ₃ H		Alkaline soils or extracts	Insensitive
		<u>NO₃-N</u>	
Reduction to NO ₂ by Cd; Griess-Ilosvay method	0.01-20	None	Very sensitive, problems with reduction step
Ion electrode	2-1400	Chloride, bromide, nitrite, iodide, sulfide, ionic strength	Less accurate than many methods
Reduction to NH ₃	1-1000	Labile amides, phosphate, nitrite	Measure NH ₃ by titration or colorimetric methods
Microdiffusion with Devarda alloy	0.1-10	Nitrite	Insensitive, slow
Ion chromatography†	0.1-50	None	Sensitive, rapid

† Added to above table by authors.

yield in this case is the plant material removed from the field during harvest. Nitrogen contained in the residue remaining in the field may be assumed to be recycled and, for the most part, sufficient to meet the N requirement of nonharvested portions of succeeding crops. This assumption is most valid in continuous production of the same crop.

The degree to which calculated crop N removal will be satisfied by a predetermined level of available soil N will be influenced by many factors. These factors include: (i) competition for N (immobilization) by soil microflora and weeds; (ii) N leaching below the effective root zone; (iii) failure of roots to grow into or absorb N from the same depth the soil was tested; (iv) cropping and N fertilization history; (v) mineralization or organic soil N; (vi) volatilization of N; (vii) crop type; (viii) crop vigor; and (ix) other growing conditions.

Hence, because the soil-crop system is dynamic, the efficiency with which crops use applied N is variable and dependent on local conditions. Hauck (1973) has reported values of 50 to 75% for crop recovery of applied N as representative of agricultural crops based on ¹⁵N studies. The upper value may be appropriate when losses by volatilization and leaching are minimal and immobilization and mineralization are in balance. Lower values are more

Table 6-2. Available soil N requirement in relation to wheat grain yield.

Yield	Crop N† removal	Available N requirement‡
	kg ha ⁻¹	
1345	30	44
2015	46	66
2690	62	88
3360	76	109
4030	92	131
4705	108	153
5375	122	175
6050	138	197
6720	153	220

† Assumes 13% crude protein.

‡ Assumes 70% N-use efficiency.

appropriate when losses or transformation to unavailable forms are expected to be high. Whatever value is used, it becomes the link between crop N removal and soil test N and allows one to calibrate the soil test. As an example, the values in Table 6-2 have been calculated for wheat (*Triticum aestivum* L.) grain at 13% crude protein ($N \times 5.7$) using an N use efficiency of 70%. If one assumes the N measured by a soil test of $\text{NO}_3\text{-N}$ or predicted from an index value will be available to meet the crop N requirement, then Table 6-2 may be used directly to interpret the soil test.

It is obvious from Table 6-2 that to use an appropriate value for the available soil N requirement, one must first identify the production level or yield goal.

V. YIELD GOAL

The yield goal is best identified by the grower. Growers best understand the degree that they can manage or control those factors other than available N which will ultimately determine crop yield (Dahnke, 1973; Dahnke et al., 1988). Growers, however, frequently do not distinguish between yield goal and yield average. This can be a costly error in lost production when weather, especially rainfall in dryland farming, varies greatly from one season to another.

Under conditions typical of the Great Plains region of the USA, the upper yield limit of nonlegumes is usually determined by the amount and frequency of rainfall during the growing season. For example, the 10-yr yield average of wheat on a particular field may be 2015 kg ha⁻¹ (30 bu acre⁻¹), but range from 1000 kg in a poor rainfall year to 3000 kg in a good rainfall year. It would seem logical to apply fertilizer N for an average yield of 2015 kg ha⁻¹ each year. In this way, N not used in poor years would be available as carry-over or residual to meet the crop needs in good years. The fallacy of this approach is that it assumes the good and poor years are normally distributed and the poor years will precede the good years. Using this approach, if several good years occur without intervening poor years, yield may be limited by lack of available N.

A more reasonable approach, and one which reduces the risk of limiting yield from lack of N, is to set the yield goal at the highest observed yield of the last 5 to 10 yr. In this instance, the common error will be that N is applied in excess of the crop requirement in poor years. Under dryland conditions, a poor year is usually a dry year, and the excess N will not be lost by leaching and should be identified by the N soil test for the next crop. An adequate, but not excessive, fertilizer rate should result in 10 to 20 kg of $\text{NO}_3\text{-N ha}^{-1}$ available at the end of the growing season in most years (Johnson, 1981).

When the crop and season allow split applications of N, the total N requirement (identified by a yield goal) may be modified based on changing conditions during the growing season. Especially in dryland farming, N use efficiency may be greatly improved by adjusting the N supply in relation to unusual soil moisture conditions that develop during the growing season.

When crops are grown under irrigation or in areas where rainfall is not limiting, the yield average may serve well as the yield goal. This assumes, of course, that N deficiency has not been a common yield limiting factor of the past.

VI. NITROGEN SOIL TEST INTERPRETATIONS

The reactions of N in a soil-plant-water system are complex involving many reactions and interactions. One approach that has been used to try to integrate the many factors involved in making a N recommendation is mathematical modeling (Tanji, 1982). The problem with this approach in a soil testing program is that to be useful the complexities have to be simplified and "at times, the simplifications are so gross that the results are not very meaningful" (Tanji, 1982). Therefore, the approaches actually used in soil testing programs are simplified and often empirical.

A. Available Nitrogen Indexes

The need for a N availability index has already been indicated by the extensive list of researchers publishing on this approach to estimating crop N needs. Since these indexes, whether biological or chemical, are indirect measures or estimates of available N they must be calibrated. The calibration usually involves field research measuring yield, N uptake or both. Most often the calibration allows one to arrive at a numerical value for available N without having actually measured it. In some instances, the estimation of available N may be circumvented by a calibration that relates the index to a N fertilizer need at a specified crop yield level.

The most common availability index is soil OM. An example of how this index is used to estimate available N adjustments is shown in Table 6-3 as used by the Univ. of Missouri (Buchholz et al., 1981). This table estimates the amount of N that will become available based on soil organic matter content, texture, cation exchange capacity, and whether a cool- or warm-

Table 6-3. Nitrogen rate adjustments used by the Univ. of Missouri based upon soil texture, organic matter (OM), and time of major crop growth (Buchholz et al., 1981).

Soil texture	Cation exchange capacity	OM	Cool-season crops	Warm-season crops
	cmol _c kg ⁻¹		— kg ha ⁻¹ (lb acre ⁻¹) —	
Sands to sandy-loams	10	0.5	11(10)	22(20)
		1.0	22(20)	45(40)
		1.5	34(30)	67(60)
Silt loams to loams	10-18	2.0	22(20)	45(40)
		3.0	34(30)	67(60)
		4.0	45(40)	90(80)
Clay loams to clays	18	2.0	11(10)	22(20)
		3.0	17(15)	34(30)
		4.0	22(20)	45(40)
		5.0	28(25)	56(50)

season crop is being produced. Interpretation of the availability index (%OM) simply consists of subtracting the amount of available N estimated from the amount of N required for a specified production level. As an example, an N requirement of 88 kg would be indicated from Table 6-2 for a wheat yield goal of 2690 kg ha⁻¹. A loam soil with 3% OM would be expected to supply 34 kg ha⁻¹ for wheat (cool-season crop). The difference between N required (88) and estimated available N (34) is the fertilizer N requirement, in this case 54 kg of N ha⁻¹.

The advantage of using an index such as percentage organic matter is that it is relatively stable from year to year. However, this is also a major disadvantage as it fails to indicate N carryover from excessive fertilization or crop failure.

B. Residual Inorganic Nitrogen

Direct measure of residual available soil N (NO₃-N) has had its greatest acceptance in arid and semiarid agricultural production. The limited rainfall of these regions lessens the change of NO₃-N loss by leaching or denitrification. Soil samples are usually taken soon after harvest (northern regions) or just before planting (southern regions) to avoid ambiguities caused by immobilization or mineralization. Thoroughness and consistency in sampling are critical to success in using the soil test. When 20 or more cores are composited for separate samples of the surface and subsoil of relatively uniform fields in monoculture, then tests results, with time, can become a useful guide to determining N fertilizer rates.

Interpretation of the NO₃-N soil test can be straightforward once the information for crops (Table 6-2) is available. The amount of available soil N indicated by the soil test is simply subtracted from the available N requirement, as determined from the yield goal. The difference is the amount of N which must be made available to the crop before or during the growing season:

$$\text{N requirement} - \text{soil test N} = \text{fertilizer N.}$$

[1]

The above calculation represents the approach which has been used in North Dakota (Dahnke, 1973) and Oklahoma (Johnson & Tucker, 1982) for interpretation of $\text{NO}_3\text{-N}$ soil test. A similar approach has been used in Nebraska (R.A. Wiese & G.W. Hergert, 1986, personal communication) for interpretation of this soil test. The Nebraska interpretation employs an equation to calculate the N requirement as a function of the yield goal, crop N content, and a constant 56 kg ha^{-1} (50 lb acre^{-1}) fertilizer N addition. This calculated N level is adjusted upward for decreasing N-use efficiency as yield goal increases. Similarly, the N requirement tables used in Oklahoma reflect a decrease in N-use efficiency at high yield levels.

C. Interpretation Adjustments

Production systems involving crop rotation and varied types and times of tillage do not lend themselves to straightforward interpretation of available-N tests. The principal problem centers around the seasonally changing conditions for mineralization and immobilization of N. Reducing the number of tillage operations and delaying incorporation of crop residues at a given N regime will promote transformation of residual N from mineral forms to organic forms. In these situations, such as changing from conventional tillage to minimum tillage, N-use efficiency will be lower until equilibrium is reached with a higher soil OM level. Available-N soil test levels will be low and responsive fertilizer N rates higher than for conventional tillage.

The concept of a small labile organic N pool (active) in equilibrium with a large stable organic N pool (passive) on the one hand and a small mineral N pool on the other hand, first proposed by Janssen (1958), helps explain the apparent shortcomings of the $\text{NO}_3\text{-N}$ soil test. Whether the active and passive pools are distinct entities or a continuum as suggested by Broadbent (1984), soil OM is a buffer against maintenance of a significant change in the level of mineral N in the soil. Consequently, excessively high rates of N fertilizer do not immediately result in high residual $\text{NO}_3\text{-N}$ soil test levels. If the level of N in the OM pool is low or the size of the OM pool is small relative to what the environment will support, then it may take several years of seemingly excessive N fertilization before significant residual N will be detected by the soil test. Jacobsen and Westerman (1988) has shown the N requirement for maximum grain yield of wheat to be 1.2 times higher for no tillage compared to conventional tillage. This also happens when the yield goal for a field, and associated N requirement, is suddenly changed from much below the potential yield to a yield which the climate and modern cultural practices can support.

Contrary to the above scenario, when the level of N in the organic pool is high and the pool is large relative to what the environment (or cultural practices) will support, then high yields and measureable residual $\text{NO}_3\text{-N}$ may occur without use of fertilizer N. Examples of this are easily demonstrated when a crop such as wheat is grown after plowing down alfalfa that has been in production 5 yr or more.

Interpretation of the N soil test is not always straightforward. However, the test can be a useful tool for identifying or monitoring adequate N fertilizer rates even in cropping systems with many variables. The keys to interpretation are understanding when during the season residual $\text{NO}_3\text{-N}$ is most apt to be present for sampling and determining the crop N requirement from a realistic yield goal. When attention is given to these factors the test has been found to have promise even outside the Great Plains region (Magdoff, 1984).

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Chapter 7

Testing Soils for Phosphorus¹

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The major purpose of testing soils for P is to determine the quantity of supplemental P required to prevent economic loss of crop value because of P deficiency. A soil test provides an index of the plant-available P in a soil which is in turn used to predict the amount of supplemental P needed.

A second purpose for testing soils for P is to monitor the quantity of available P present over time. This information is useful for evaluation of fertilization practices and in making decisions about waste disposal.

Phosphorus exists in soils in a multitude of chemical forms. These all contribute to varying extents to the plant-available pool. The quantity of plant-available P is not a distinct value for a given soil. It varies with several plant root characteristics and with environmental conditions that influence both soil and plant parameters. Therefore, predicting the quantity of plant-available P in a soil is no small task. However, several excellent P extraction procedures have been developed that correlate well with P uptake in controlled environments. It is the intent of the following discussion to review these facets of testing soils for P including interpretation of the test results. In the process, an attempt will be made to indicate what existing soil test methodology can and cannot do.

I. SOIL PHOSPHORUS

The transformations of applied P occur within a framework of soil P forms and reactions that can be described in a general way as the P cycle (Smeck, 1985). An example is provided in Fig. 7-1. The generally low level of P in the solution phase has led to much work describing the relationships of solution P, the pool from which the root draws the plant's P nutrition, to the other P pools interacting with solution phase P (Olsen et al., 1977;

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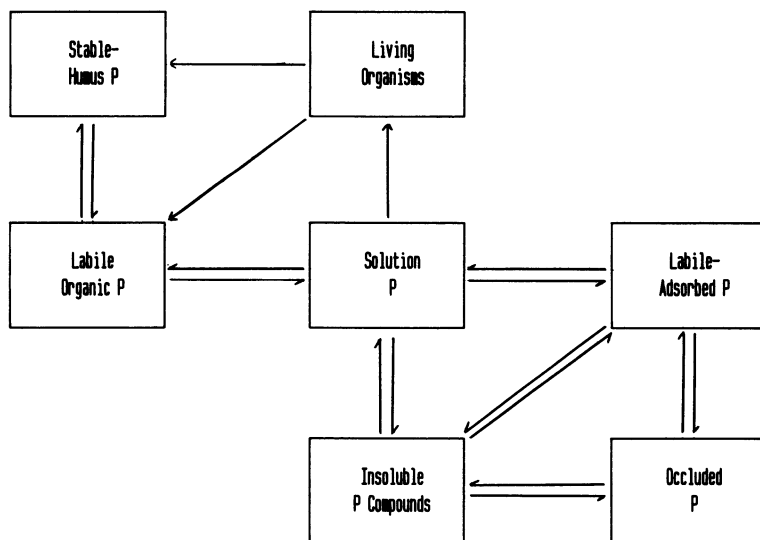


Fig. 7-1. Possible P transformations. (After White, 1980; Barrow, 1983; and Smeck, 1985.)

Sample et al., 1980). While much of the soil science literature has concentrated on inorganic P transformations, there would appear to be a growing interest in organic P transformations as well (Dalal, 1977; Anderson, 1980). This seems to reflect a desire to understand soil P availability as a part of the agro-ecosystem, a marriage of agricultural and ecological research emphases (Smeck, 1985).

This discussion will touch upon all the pools in Fig. 7-1, but with an emphasis on those aspects important to soil testing. Further, the divisions among the inorganic solid phases is more than a little arbitrary, given the heterogeneity of soil components. The removal of P from soil solution subsequent to soluble fertilizer P addition is more likely a continuum of processes, from adsorption to precipitation, that results in a continuum of chemical states (i.e., adsorbed, chemisorbed, amorphous-crystalline-occluded, precipitated), for the transformed P (Sample et al., 1980; Barber, 1984).

When describing the status of P in soils, it becomes apparent that the definitions of the various forms (pools) of P are dependent on the investigatory techniques chosen. Therefore, this discussion will use investigatory techniques as a framework of presentation.

A. Adsorbed Forms of Phosphorus

Schofield (1955) argued that continued research emphasis on the action of P extracting solutions on soils would not lead to a better understanding of the fundamental chemistry of available soil P. Since Schofield's paper, there have been many studies regarding the mechanism(s) of P retention by soil carbonates, silicates and hydrous oxide clay minerals, and soil organic

matter. As the literature on this topic is voluminous, only representative reports will be cited here.

Adsorbed P is often equated with the labile soil phosphate most available to plant roots; i.e., most readily in equilibrium with the soil solution. Phosphorus adsorption is delineated from P precipitation in that the suspension's initial solution phase composition does not exceed the solubility product of any *known* P compound. One approach to measuring this soil P fraction is the use of ^{32}P in isotopic exchange studies (Olsen & Khasawneh, 1980; Wolf et al., 1986). Though this technique is somewhat more sophisticated, the extension of the kinetic information obtained to an understanding of actual P-bonding mechanisms has proved illusive as results are highly dependent on method and the mathematical formula used (White, 1976; Olsen & Khasawneh, 1980). This problem led Wolf et al. (1986) to conclude that isotopic exchange should not be used on soils with high amorphous Fe contents and consequently higher P fixation tendencies.

Adsorption curves (rather than isotherms, see White, 1980) and the equations to describe them are derived from reacting minerals and soils with solutions at various P concentrations and have been a popular means of describing P adsorption and proposing P bonding mechanisms (Barrow, 1980b; Olsen & Khasawneh, 1980; Sample et al., 1980). Because the technique is a simple one, adsorption curves have been used on the largest number of soils and minerals.

Uehara and Gillman (1981) proposed that differences in P adsorption could be accounted for by differences in: (i) specific surface; (ii) colloid capacity to occlude P; (iii) concentration or type of species, usually anions, that compete with P by adsorbing to, or dissolving, the adsorption site; and (iv) colloid surface reactivity.

Differences in P adsorption because of surface reactivity are largely the result of the reactions of P with Al, Ca, and Fe cations that are themselves part of, or strongly sorbed to, colloid surfaces (Wild, 1950; Thomas & Peaslee, 1973). Such differences separate soils into broad classes on the basis of the reactions of their colloid suite with soluble P. Geographically, as rainfall, temperature, and weathering increase, the role of Ca in P adsorption reactions diminishes and that of Al and Fe rises.

On the most highly weathered soils, P adsorption is thought to be largely related to the presence of hydrous Al and Fe oxides. In studies with pure oxides, P adsorption curves often resolve into at least two and sometimes three regions of adsorbing surface where distinctly different bonding mechanisms are thought operative (Bache, 1964; Ryden et al., 1977). White (1980) has been critical of such an approach to mechanism determination, arguing that two (or more) surface models are empirical and no better than models that assume a continuous spectrum of adsorption strength. This latter feature would be especially true of heterogeneous mixtures (soils).

Data from traditional P adsorption curves have been combined with additional information on changes in surface charge, solution pH, and concentrations of both counter ions and background electrolytes to better describe P bonding mechanisms on hydrous oxides of Al and Fe as well as other miner-

als (White, 1980). The ligand exchange of phosphate for surface aquo and hydroxyl groups bonded to Al and Fe has been shown to result in monodentate, bidentate, or binuclear forms of adsorbed P (Fig. 7-2a). The bidentate and binuclear types of bonding should be less reversible than monodentate. Hingston et al. (1974) have proposed that P sorbed to Al is more labile than that adsorbed to Fe. Ainsworth et al. (1985) demonstrated that ^{32}P -isotopic exchange rates on goethite increased with Al substitution for Fe in the hydrous oxide lattice.

As suspension pH rises, phosphate adsorption is less favored by the greater negative charge at the oxide surface (Fig. 7-2b) and the reduced polarization of the metal-oxygen bond. Martin and Smart (1987) used x-ray photoelectron spectroscopy (XPS) to confirm both the pH dependence and binuclear nature of P adsorption to goethite. Goldberg and Spósito (1985) reviewed the evidence for multiple attachment of phosphate to hydroxylated surfaces and found it wanting, primarily because the analytical techniques used to confirm the existence of binuclear complexation (XPS and infrared spectroscopy among them) required dry, severely evacuated samples that are unlike those same colloid surfaces in soils where water is present.

Adsorption of P in lime amended, acid, oxidic soils has not always behaved as predicted from pure oxide models; P sorption increasing, rather than decreasing, with increasing pH (Amarasiri & Olsen, 1973; Mokuwunye, 1975; Friesen et al., 1980). Haynes (1983), using the E horizon of a Spodosol, was able to reverse increased P sorption with greater pH by air drying the soil samples after lime addition. Sims and Ellis (1983a) found that as the lime incubation time progressed the energy of subsequent adsorbed P bonding was reduced even though the adsorption maxima increased, regardless of whether the limed soil samples were subjected to wet and dry cycles during incubation.

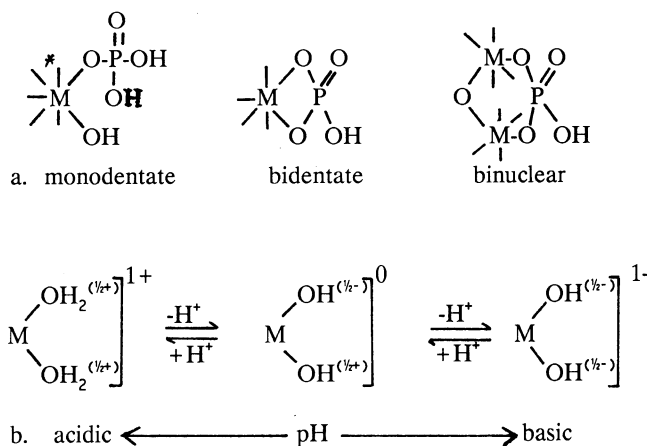


Fig. 7-2. Types of P bonding (a) and pH-dependent surface charge characteristics (b) associated with hydrous oxides. (After Sample et al., 1980; Uehara & Gillman, 1981; and White, 1980.) *M = Al, Fe.

Closer examination of this phenomena on model systems using Al-resins (Robarge & Corey, 1979), Al-gels (Sims & Ellis, 1983b), Al-peats (Bloom, 1981; White & Thomas, 1981), and acid montmorillonites (Coleman et al., 1960; Traina et al., 1986a, b) indicates that the existence of sufficient exchangeable Al^{3+} prior to liming, the formation of amorphous hydroxy-Al polymers after liming, and the reaction of these polymers with P to form sorbed/precipitated complexes of an OH/Al/P composition near 2:1:1 is the likely chain of events. Haynes (1984) summarized the different P sorption response patterns observed in terms of the loss of surface area because of further crystallization of the hydroxy-Al with both aging and drying after liming. Haynes (1984) also notes that further work is needed as both inorganic and organic anions have been reported to slow hydroxy-Al crystallization and this could result in increased P adsorption despite drying.

Exchangeable bases and silicate clay minerals strongly influence P adsorption in soils of weak to moderate acidity (minimal exchangeable Al). It is widely known that P adsorption increases as both counter-ion valence and ionic strength increase in silicate clay systems (Sample et al., 1980; White, 1980; Velayutham, 1980). Some P is likely adsorbed at the broken edges of the silicate clay lattice by ligand exchange at Al (White, 1980).

Though Ca has long been known to enhance P adsorption, the clay-Ca-P linkage model was thought inappropriate (Velayutham, 1980). Further observations on Ca enhanced P adsorption in both silicate and oxide clay systems (Helyar et al., 1976; Haynes, 1983; Smillie et al., 1987) have led to the proposal that Ca and P sorption are complementary (Smillie et al., 1987), interacting as a Ca-P surface complex (Helyar et al., 1976). This mechanism is distinct from that proposed to explain the role of Ca on P fixation in acid soils by the displacement and hydrolysis of reactive Al (Robarge & Corey, 1979; Traina et al., 1986b).

In calcareous soils P adsorption occurs on soil carbonates, whose impurities result in greater specific surface than that of pure calcite (White, 1980). Though adsorption is thought to dominate the initial reaction of soluble P with calcareous soils at low P concentrations, precipitation of P as a Ca-P compound is the ultimate fate (Barrow, 1980a). The adsorbed P sites serve as nucleation points for the formation of a basic Ca-P compound (White, 1980). There is still some question regarding the initial Ca-P compound formed subsequent to P adsorption (Sample et al., 1980; Freeman & Rowell, 1981).

B. Phosphorous Desorption

No discussion of P adsorption is complete without some reference to P desorption. Phosphorus desorption curves often do not coincide with their adsorption counterparts (Fig. 7-3) resulting in what has been termed *P sorption hysteresis* (Uehara & Gillman, 1981). This irreversibility or fixation of adsorbed P has been ascribed to several processes, including precipitation (Veith & Sposito, 1977), occlusion (Uehara & Gillman, 1981), solid state diffusion (Barrow, 1983) and bidentate or binuclear bonding with the colloid surface (Hingston et al., 1974; Taylor & Ellis, 1978).

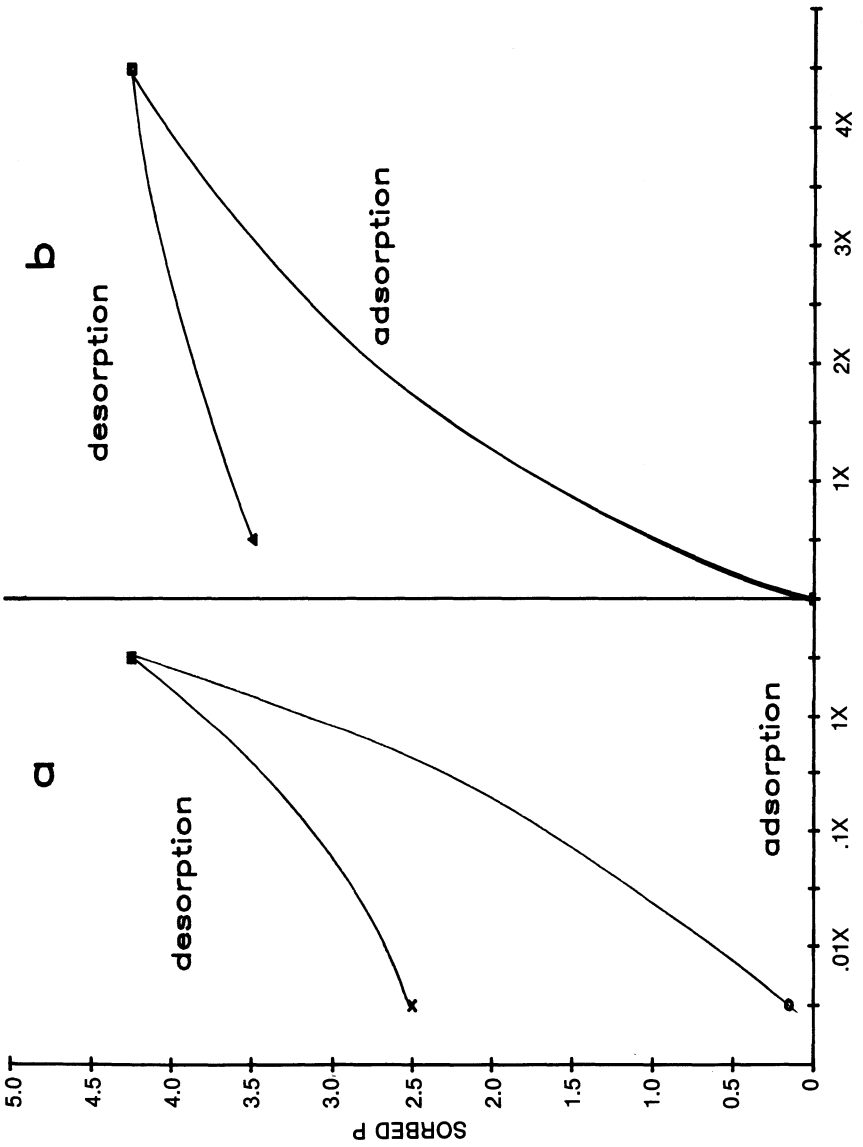


Fig. 7-3. Idealized P sorption-desorption curves: a = semilog, b = linear. (After Uehara & Gillman, 1981; and Barrow, 1983.)

It is clear that P sorption hysteresis is a function of time, initial P application rate, colloid type, and investigative approach (Barrow, 1980b). Anion exchange resins have been used to study P desorption (Bache & Ireland, 1980; Olsen & Khasawneh, 1980; Wolf et al., 1986), as have adsorption-desorption curves (White, 1980; Barrow, 1983).

Desorption curves in laboratory solutions often do not match those determined on the basis of crop removal (White, 1980). This would indicate that our knowledge of plant root effects on the abiotic pools and processes outlined in Fig. 7-1 is still incomplete. As more knowledge on P bonding mechanisms is acquired, our understanding of soil P release should improve as well.

C. Precipitated Forms of Phosphorus

When P fertilizer is applied to soil as highly water soluble granules or as droplets of a suspension or solution the nearby soil particles are awash in a solution of very high P concentration. The solubility product of one or more P compounds is likely to be exceeded and precipitation ensues (Sample et al., 1980). Many different types of reaction products are possible, though most involve Al, Ca, Fe, Mg, NH_4 or K as the counter ion to HPO_4 or PO_4 (Sample et al., 1980).

Initial reaction products are likely to undergo transformation to less soluble forms with time. Thomas and Peaslee (1973), in their summary on soil P testing, came to three general conclusions no less valid today:

1. The quantity of inorganic P in any given soil is related to the soil's parent material.
2. The form of P present, whether bonded to Al, Ca, or Fe, is related to the degree of weathering.
3. Added soluble P will eventually be found in precipitated forms not unlike those of native P (Fig. 7-4).

In calcareous soils, soluble P should ultimately be transformed to an apatite, though the presence of free iron oxides in these soils can complicate the outcome (Ryan et al., 1985). In most acid soils, iron phosphates are the least soluble, most stable form of soil P.

Two approaches to the understanding of solid phase soil P are in general use, solubility product-chemical potential evaluations and chemical fractionations of soil P. Evaluation of solid phase P compounds in soil using solubility or ion activity products is thoroughly discussed by Lindsay and Vlek (1977). In general, the composition of the solution in equilibrium with the soil (mineral) is determined and that point plotted on a phase diagram (Fig. 7-5). If the point lies above the nearest line, then the solution is supersaturated relative to that mineral and precipitation can occur. A point below the line indicates undersaturation of the solution and dissolution is plausible.

This approach has been used to characterize several soil and fertilizer P transformations. Olsen et al. (1977, 1983) reported that cropping 23 calcareous and alkaline soils of eastern Colorado resulted in the dissolution and

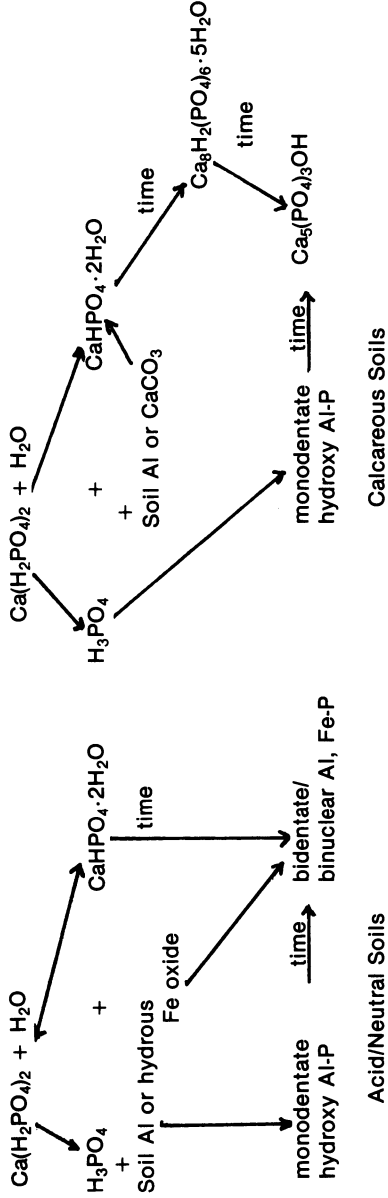


Fig. 7-4. Transformations of monocalcium phosphate in soils. (Modified from Thomas & Peaslee, 1973).

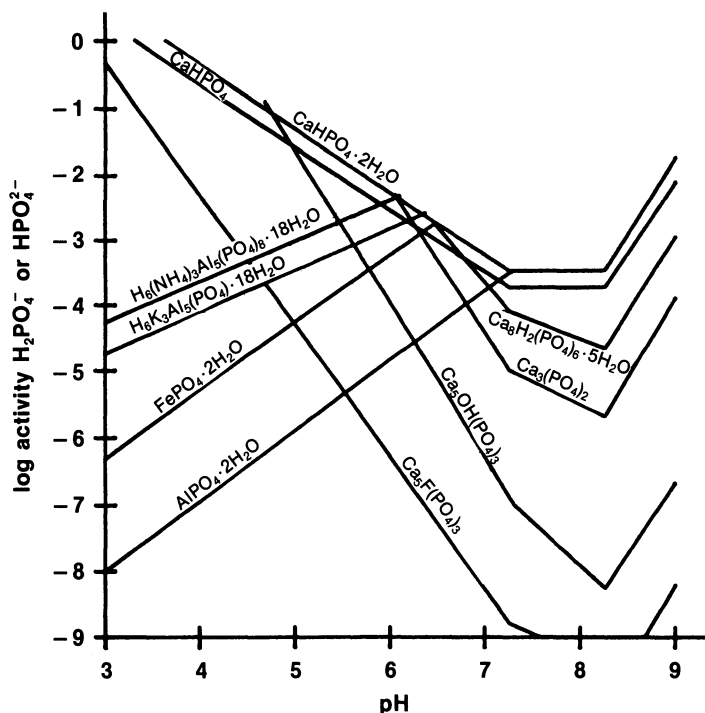


Fig. 7-5. A "unified" phase diagram for several phosphate compounds. (Taken from Lindsay & Vlek, 1977.)

plant utilization of octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$] and suggested that soils exhibiting equilibrium with this P compound would have a high P status. A similar observation was reported by Adepoju et al. (1986) on 12 southern California soils. Fixen et al. (1983) and Havlin and Westfall (1984) concluded that P solubility was being controlled by β -tricalcium phosphate [$\beta\text{-Ca}_3(\text{PO}_4)_2$] in two calcareous soils with reduced P availability.

Phase diagrams are usually used in soil P systems at or near equilibrium, but not always. Hanson and Westfall (1985) used such diagrams to follow the reaction(s) of injected ammonium polyphosphate over a 90-d sampling period. They concluded that superior plant P nutrition from dual injection of NH_3 and ammonium polyphosphate resulted from the high initial pH, which caused the formation of readily plant-available calcium phosphate reaction products in their moderately acid soils.

Using phase diagrams to determine the dominant stable soil P compound has generally been more successful in calcareous soils. Harrison and Adams (1987) could not determine whether any P mineral was controlling solution phase P concentrations in an Ultisol limed to several pH levels and P fertilized at several rates. This may be because adsorbed P is more important over a comparable time frame in noncalcareous soils (Barrow, 1980a). Blanchar and Stearman (1984) have demonstrated that the combination of ion activity from the solution phase with an estimate of the activity of P sorbed

to soil Al compounds (the solid phase P activity) could help predict P solubility subsequent to P addition on eight noncalcareous Missouri soils.

Ion activity product-phase diagrams assume that the P minerals indicated on the phase diagram are indeed those of importance in a particular soil-fertilizer P system. Soil P compounds may contain impurities or be sufficiently amorphous so as to significantly change the solubility product from that posted in the literature for a pure, crystalline P compound. In addition, although there may be several soil P compounds in a sample, only the most soluble will be determined. Organic P compounds are not determined. Most importantly, the technique assumes the system is at or near equilibrium, even if only metastable, between soil and extract. Solid phase transformations may occur very slowly and the extract can be far from equilibrium (Olsen & Khasawneh, 1980; Sample et al., 1980).

Soil P fractionation makes use of chemical extraction/digestion techniques, applied in sequence to a single sample, to strip away different classes of P compounds one group at a time. The most popular approach is that of Chang and Jackson (1957), which first separated soluble P using NH_4Cl , then Al-P compounds with NH_4F (pH 7.0). The sample is then subjected to NaOH extraction for Fe-P forms and H_2SO_4 dissolution for Ca-P minerals. The final step is reduction of Fe in insoluble compounds with $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of citrate to release occluded, "reductant soluble" soil P. Modifications to the basic scheme are detailed by Olsen and Khasawneh (1980) and Olsen and Sommers (1982). Other soil P fractionation techniques involve fewer steps (Tiessen & Stewart, 1983; Sharpley, 1986; Weil et al., 1988) or reflect a greater emphasis on the organic P fraction (Hedley et al., 1982).

Fractionation has been put to several purposes. Ryan et al. (1985) found that P sorption in several calcareous soils from Lebanon was related more to the presence of free iron oxides than to soil carbonates. Enwezor (1977) related plant growth to each of several soil P fractions, as well as other indices of plant-available P, and found all fractions accounted, to some extent, for plant performance. The direct relationship between many of the chemical constituents used in fractionation and those used as plant-available P extractants has led to many such comparisons.

McCallister et al. (1987) used a fractionation scheme to follow transformation(s) of applied P on four Nebraska Mollisols after 12 yr of cropping at several P-fertilization rates. Annual P application resulted in greater fixed P than biennial applications at equivalent (over time) fertilization rates. This observation was not buttressed by greater crop response to biennial P applications. Hooker et al. (1980) used fractionation in a similar way on five calcareous soils, finding that the added P initially sorbed by Fe and Al bearing surfaces was then lost to less soluble forms more quickly when the soil carbonate level was $>18 \text{ g kg}^{-1}$ (1.8%).

Fractionation-extraction techniques are still the approach of choice in many evaluations of soil organic P transformations, whether because of cultivation (Hedley et al., 1982; Dick, 1983; Tiessen & Stewart, 1983; Sharpley & Smith, 1985; Weil et al., 1988), crop rotation (O'Halloran et al., 1987), or soil genesis/weathering (Smeck, 1985; Sharpley et al., 1987). These studies

are facilitated by newly proposed fractionation sequences that purport to better describe organic P fractions (Bowman & Cole, 1978; Hedley et al., 1982).

Soil P fractionation has been sharply criticized by Olsen and Khasawneh (1980), who argue that such extractions are rarely selective, incapable of distinguishing among metastable intermediate reaction products, and overly dependent on the simplistic classification of soil P as Ca-P, Fe-P, and Al-P. Nevertheless, much P research continues to rely on such procedures.

D. Organic Phosphorus

There have been several recent reviews regarding organic P. The reader may refer to Dalal (1977) and Anderson (1980) for more detailed information on this subject. Organic P is an important reservoir for soil P, ranging from 20 to 80% of total soil P (Dalal, 1977). Organic P compounds are largely phosphate esters. Major classes of these, in order of decreasing resistance to mineralization (decreasing quantity found in soils) are: inositol phosphates, phospholipids, and the nucleic acids (Dalal, 1977; Anderson, 1980). About one-half of the organic P fraction consists of unidentified compounds. In soils with substantial levels of organic matter, soluble organic P may constitute one-half of the P found in the soil solution (Barber, 1984). Despite such observations, the role of organic P in crop P nutrition has often been viewed as a small one.

New information on nutrient cycling (McGill & Cole, 1981; Smeck, 1985) has placed greater emphasis on organic P and related transformations. Of particular interest to soil testing are agro-ecosystems where organic P does indeed play a critical role in plant (and animal) P nutrition. Some of these include pastures-grasslands (Rixon, 1966; Cole et al., 1977; Sharpley, 1985) and agricultural soils in parts of Africa (Adepetu & Corey, 1976; Enwezor, 1977; Anderson, 1980). In several of these studies, organic P has been somewhat related to extractable, soil test P (Adepetu & Corey, 1976; Enwezor, 1977; Sharpley, 1985; Sharpley et al., 1987). This relationship may warrant special consideration in more highly weathered soils (Sharpley et al., 1987).

II. FACTORS AFFECTING PLANT AVAILABILITY OF SOIL PHOSPHORUS

The quantity of P available to plants at any instance is determined by both soil and plant properties. These properties are in turn influenced by several environmental conditions.

A. Soil Properties

Classically, the factors defining soil P availability have been intensity (soil solution P concentration); quantity (amount of solid phase P that is capable of entering the soil solution); capacity ($\partial Q/\partial I$); dissolution/desorp-

tion rate; and diffusion (Dalal & Hallsworth, 1976). These factors are interdependent and influenced by the relative saturation of the P adsorption maximum (Gunary & Sutton, 1967). This relationship had led to several studies where phosphate sorption or relative saturation were successfully used to predict fertilizer P requirements (Woodruff & Kamprath, 1965; Peaslee & Fox, 1978). Due to the time and labor involved in such determinations, however, these methods are generally not acceptable for routine diagnostic laboratories.

More recently, the classical factors have been recombined as part of a mechanistic model for nutrient uptake that involves both soil and plant parameters (Claassen & Barber, 1976). In this approach, the soil P factors are C_{li} , the initial concentration in the soil solution; b , the buffer power; and De , the effective diffusion coefficient. The relationship between these factors for a Raub silt loam (fine-silty, mixed, mesic Aquic Argiudolls) is shown in Fig. 7-6. The model has accurately predicted P uptake in both growth chambers and in the field (Schenk & Barber, 1980; MacKay & Barber, 1985b).

Soil pH exerts indirect effects on soil P availability through the factors mentioned previously. Larsen et al. (1965) showed that the half-life of labile P from fertilizer additions decreased significantly as pH increased for non-calcareous mineral soils with initial pH levels from 5.8 to 8.0. Formation of apatitic minerals was cited as a possible cause. An equilibration study of a Lucedale sandy loam soil (fine-loamy, siliceous, thermic Rhodic Paleudults) from Alabama with an initial pH of 5.2, showed that soil solution P levels increased with liming up to a pH of 5.7, then decreased at 6.2 and decreased further at 6.6 provided the lime was added before the P (Soltanpour et al., 1974). Adams (1984) later pointed out that the increase in P solubility from liming at the lower pH levels was likely due to precipitation of exchangeable Al^{3+} as suggested by Coleman et al. (1960).

Such factors as Fe content, carbonate content, carbonate specific surface area, clay content, and organic P content, have been shown to also indirectly affect the availability of soil P (Soper & El Bagouri, 1964; Fixen & Ludwick, 1982; Holford, 1977; Cole et al., 1977). These effects have been discussed previously.

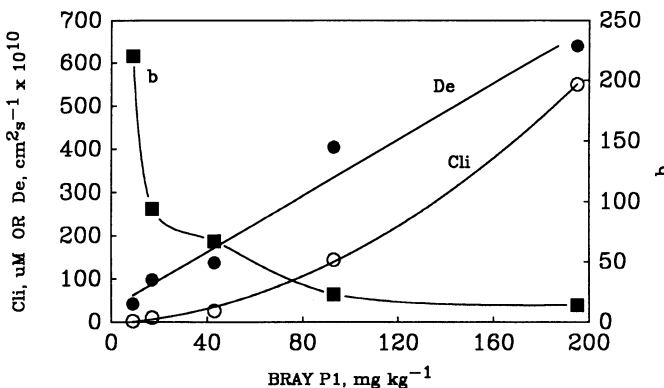


Fig. 7-6. Soil P supply parameters for a Raub silt loam. (Modified from Yao & Barber, 1986.)

B. Plant Characteristics

Generally < 1% of the soil volume is occupied by plant roots (Barber, 1984). Therefore, any factor influencing root system size or morphology will likely effect the quantity of soil P that is available to a plant. Simulated sensitivity analysis has demonstrated the large impact rate of root elongation has on P uptake (Silberbush & Barber, 1983).

Characteristics of individual roots, such as root hair length and density (Itoh & Barber, 1983); mycorrhiza infection (Tinker, 1984); and uptake kinetic parameters (Anghinoni et al., 1981) also influence a plant's ability to remove P from soils. Such differences in root system characteristics and individual root properties, together with differences in root/shoot ratios and other characteristics, are responsible for the differing P management requirements of species and, in some cases, cultivars (Baligar & Barber, 1979).

C. Environmental Conditions

Many of the soil and plant parameters discussed above are influenced by environmental conditions such as temperature and moisture. Temperature directly influences soil P in several ways. In a review article, Sutton (1969) described studies demonstrating increases in isotopically dilutable P, labile P, and resin exchangeable P with increased temperature. Regression studies have indicated that the importance of organic P in predicting P availability increases with temperature (Eid et al., 1951). A Nebraska study on the effect of time of sampling on several soil test P measurements revealed that soil test levels were approximately 25% higher in the early spring than they were in the preceding fall. The authors concluded that this change was due to environmental conditions unfavorable for P mineralization and replacement of P used by plants prior to the fall sampling (Olson et al., 1954). Temperature also influences several of the plant characteristics mentioned earlier. Root elongation rates and root uptake kinetic parameters are sensitive to temperature changes.

Many studies have been conducted on the effect of soil moisture on P availability and response to applied P. Power et al. (1961) reported that 53% of the variation in fertilizer response of spring wheat (*Triticum aestivum* L.) on medium P soils was because of variation in available soil moisture. Grain yield response to seed placed P increased 29 kg ha⁻¹ for every centimeter increase in available soil water at seeding (1.09 bu in.⁻¹). If precipitation between tillering and heading growth stages was also considered, 81% of the response variation was explained.

A greenhouse experiment on millet demonstrated that P uptake increased as soil moisture increased at a soil temperature of 27°C, but not at 16°C (Mack & Barber, 1960). This type of interaction between environmental factors has frequently made it difficult to understand P response under field conditions.

More recent investigations on the effects of soil moisture on root growth and P uptake have aided our understanding of how moisture content and

plant P uptake are related. MacKay and Barber (1985a, b) showed that P uptake by corn (*Zea mays* L.) decreased at soil moisture contents above and below field capacity because of effects on both P diffusion and root growth rates. Uptake of P dropped more than did total plant weight when soil moisture was decreased below field capacity indicating that the decrease in uptake was not likely due only to decreased demand. They also demonstrated that the negative effects of low soil moisture contents may be partially offset by increases in root hair growth. A sensitivity analysis by these authors using the Claassen-Barber (1976) simulation model indicated that root growth rate was the uptake parameter most influenced by soil moisture content (Barber & MacKay, 1985).

D. The Role of Labile Phosphorus

Clearly, the quantity of plant-available P in a soil is a dynamic entity that can only be crudely estimated by any soil extractant. Our greatest reasonable expectation of a soil P extractant is that it be highly correlated with labile P. The definition of labile P is discussed at length by Olsen and Khasawneh (1980). Conceptually, labile P is soil P in rapid equilibrium with soil solution P and is usually assumed to be equivalent to the fraction of soil P which is isotopically exchangeable with ^{32}P within a given period.

Even if a soil extractant is perfectly correlated with labile P, it would likely explain only a fraction of the P response variability in the field when diverse soils, climatic conditions, and cultural practices are included. The quantity of labile P in a soil is just one of several factors that determine the plant availability of soil P.

III. DETERMINING PLANT-AVAILABLE SOIL PHOSPHORUS

Based on the discussion in the previous section, it is obvious that labile and plant-available P are not directly superimposable concepts, not precisely defined (nor observed) as discrete portions of soil P, and depend on time and technique (Olsen & Khasawneh, 1980). While it is evident that techniques such as resin desorption, isotopic exchange, and quantity/intensity curve formation offer alternative approaches for plant-available P assessment, none have proven uncomplicated enough in practice, theory, or interpretation to make serious inroads into common soil test usage. The overwhelmingly largest fraction of soil samples are tested for available P by extraction with dilute solutions.

A. Selection Criterion for Available Soil Phosphorus Extractions

Kamprath and Watson (1980) have outlined the objectives of P soil tests. First, the soil test result should place the sample (field) in a predetermined group or category to make a fertilizer P recommendation. The terms low, medium, and high equate to one such classification system. Second, the test

result should indicate the likelihood of an economic return to fertilizer use. This goes hand-in-hand with the classification system; a low test result indicating a high probability of response and vice-versa. Additional economic information on fertilizer and commodity prices is required to successfully meet this goal. Third, the soil test result should be directly related to the soil's P supply capability. This direct relationship, in addition to indicating whether fertilizer is needed, can be used to calculate the rate of fertilizer P to be added. This latter calculation assumes a knowledge of how added soluble P changes P test values for soils of the region(s) served by the testing laboratory.

Criterion for a suitable extractant have been detailed in several reports. Thomas and Peaslee (1973) felt that the extractant should (i) remove a reproducible and consistent proportion of the soil's plant-available P and (ii) reflect the extent and nature of reactions between soils and added P. Barrow (1980b) also felt that a soil test was an integration of several factors affecting soil P status into one numerical value. He included soil P buffering capacity with P quantity and soil P reaction time in his list of factors. Holford (1980) demonstrated that soil test P removal should be inversely related to buffer capacity, though this depended on whether plant-available P was being made available via desorption or dissolution. Kamprath and Watson (1980) noted that the extractant should (i) extract a proportionate fraction of plant-available P from soils differing in other properties; (ii) the procedure should work with reasonable accuracy and speed; and (iii) the soil test P value determined should be correlated with crop growth response to P or P uptake.

B. Extractant Mode of Action

Though Thomas and Peaslee (1973) state that several soil test extractants were developed empirically prior to the release of the P fractionation method (Chang & Jackson, 1957), the fractionation technique is often the basis of explaining extractant mode of action. A knowledge of extractant-soil interaction chemistry is most useful when understanding divergent extractant behavior because of (i) differences in available P sources on soils of otherwise similar properties (Smyth & Sanchez, 1982; Admont et al., 1986) or (ii) differences among soils fertilized with a common P source (Varvel et al., 1981).

There has been a divergence between soil P chemistry and soil P testing. More is known about soil P bonding than is used in soil testing. Little additional information exists regarding the bonding of P removed by common chemical extractants. In terms of new definitions of soil P, are we extracting monodentate, binuclear, amorphous occluded or crystalline P compounds? There is a need for detailed studies on the nucleophilic/electrophilic behavior of extractant constituents on P sorbed to model surface materials. Progress in this area is not furthered by the highly empirical approach seemingly being employed in the development of multiple element extraction techniques.

Kamprath and Watson (1980) proposed four general reactions contributing to P release from soil by extractants. These were (i) acid dissolution, (ii) anion exchange, (iii) cation complexation, and (iv) cation hydrolysis.

Both strong (HCl, HNO₃, and H₂SO₄) and weak (acetic, citric, and lactic) acids have been used to extract soil P. Acid concentrations used are usually low, resulting in extracting solution pH values generally below 5 for weak acid extractants, and near pH 2 for strong acid extractants. All three inorganic P forms are dissolved to some extent by acids, where Ca-P > Al-P > Fe-P describes the decreasing order of solubility (Mehlich, 1978a). If the duration of soil-extractant contact is kept short, Fe-P dissolution is minimized (Thomas & Peaslee, 1973).

Other anions can replace adsorbed P if their size, binding strength, or concentrations are appropriate to the quantity and type of colloid surface present. They also serve to minimize readsorption of P if the extraction time is kept short (5–10 min). Examples are acetate, bicarbonate, citrate, lactate, and sulfate (Mehlich, 1978a; Kamprath & Watson, 1980).

Fluoride and certain organic anions (citrate and lactate) complex Al. Extractants containing these anions release P from Al-P compounds. Bicarbonate precipitates soluble Ca as CaCO₃, causing release of Ca-P. Fluoride also results in CaHPO₄ dissolution with concomitant precipitation of CaF₂. Thomas and Peaslee (1973) argue that bicarbonate (HCO₃) and F remove similar soil P forms, though F is more competitive/aggressive.

The distinction between anion competition at the colloid surface and ligand competition in the solution is probably artificial as the same cations (Al, Ca, and Fe) and anions (acetate and sulfate) are often involved. Cation hydrolysis occurs at high pH values where the hydroxyl anion (OH) dissolves a portion of the Al-P and Fe-P by hydrolysis of Al and Fe. This is a specific form of the anion/ligand competition reactions described earlier. Extractions using buffered HCO₃ solutions can remove some Al-P and Fe-P from soils because of their higher OH concentrations (Maida, 1978).

Conflicting claims regarding the selectivity of the fractionation technique (Thomas & Peaslee, 1973; Olsen & Khasawneh, 1980) can be extended to discussions on the specificity of a particular extractant for particular forms of soil P. Even the simplest P extracting solutions offer more than one mode of action in P removal. Chang and Juo (1963) observed that the distribution of soil P amongst the several fractions affected the correlation of extractable P for a particular method with a particular soil P fraction. As the soil P becomes distributed more evenly amongst more fractions the relationship between any P extraction and a P fraction for a given soil falters. This also applies to situations where soil diversity is so great as to require "grouping" before meaningful relationships between soil P extractions and soil P fractions can be undertaken (Sen Tran & Giroux, 1985; Sharpley et al., 1987).

The release of P from soil organic compounds can be a significant source of plant-available P (Adepetu & Corey, 1976; Enwezor, 1977; Sharpley, 1985). The extraction of available inorganic P from such soils has been shown to be related to the organic P fraction. Again, the exact mechanism is unknown, but the most successful extractant contains both fluoride and dilute acid.

The implication is that either acid hydrolysis of organic P esters or breakup of organo-metallic (Al and Fe) bound P is occurring. Sharpley (1985) reported that the organic P-extractable P relationship for a given soil was strongly related to concurrently extractable inorganic P concentrations.

The analytical outcome (amount of P removed) of any extraction is determined by technique factors in addition to the chemical composition of the extracting solution. Increasing the solution to soil ratio can increase P extractability (Randall & Grava, 1971) as can lengthening the extraction time (Breland & Sierra, 1962). Raising or lowering the concentration(s) of one or more solution constituents can markedly influence soil P removal (Thomas & Peaslee, 1973). These kinds of differences in soil testing technique as well as other, more subtle, factors such as shaking speed, extraction container size and shape, and sample size contribute to such variation (Grava, 1975).

C. Extractants Used to Determine Available Soil Phosphorus

Extractants commonly used in soil test laboratories for both past and present P evaluation are listed in Table 7-1. Earlier surveys of procedures in use in the USA indicate that the Bray P₁, Mehlich I, and Olsen extractions were often used (Bingham, 1962; Jones, 1973). A more recent survey suggests that the Mehlich III procedure is gaining wider acceptance (SRSTIEG, 1984).

Though it is generally accepted that acid extractants are more appropriate for acid soils and bicarbonate containing reagents more suitable for calcareous soils, there is evidence that the Olsen (NaHCO₃) extraction performs reasonably well on acid soils (Farina & Channon, 1979; Smyth & Sanchez, 1982). This may be related to release of P from Fe surfaces to both plants

Table 7-1. Soil test extractants commonly used to determine available soil P.

Extractant name(s)	Extractant composition	Reference
AB-DTPA	1 M NH ₄ HCO ₃ + 0.005 M DTPA - pH 7.5	Soltanpour & Schwab, 1977
Bray P ₁	0.03 M NH ₄ F + 0.025 M HCl	Bray & Kurtz, 1945
Bray P ₂	0.03 M NH ₄ F + 0.1 M HCl	Bray & Kurtz, 1945
Citric acid	1% citric acid	Dyer, 1894
Egner	0.01 M Ca lactate + 0.02 M HCl	Egner et al., 1960
ISFEIP (Hunter)	0.25 M NaHCO ₃ + 0.01 M NH ₄ F + 0.01 M EDTA - pH 8.5	ISFEIP, 1972
Mehlich I (Double acid, North Carolina)	0.05 M HCl + 0.0125 M H ₂ SO ₄	Mehlich, 1953
Mehlich II	0.015 M NH ₄ F + 0.2 M CH ₃ COOH 0.2 M NH ₄ Cl + 0.012 M HCl	Mehlich, 1978b
Mehlich III	0.015 M NH ₄ F + 0.2 M CH ₃ COOH 0.25 M NH ₄ NO ₃ + 0.013 M HNO ₃	Mehlich, 1984
Morgan	0.54 M CH ₃ COOH + 0.7 M NaC ₂ H ₃ O ₂ - pH 4.8	Morgan, 1941
Olsen	0.5 M NaHCO ₃ - pH 8.5	Olsen et al., 1954
Truog	0.001 M H ₂ SO ₄ + (NH ₄) ₂ SO ₄ - pH 3	Truog, 1930

and HCO_3 solutions in these soils (Maida, 1978). Maida (1978) also reported that the Bray P_1 procedure did not seem to recover Fe-P, but rather Al-P and Ca-P, on the Malawi soils studied.

Michaelson and Ping (1986) reported that the amount of P recovered by weak acid-fluoride extractants (Mehlich II, III, and Bray P_1) was strongly related to oxalate extractable Al + Fe in 10 soils. They also found Mehlich III to be superior to the other extractants when volcanic ash and loess-derived soils were pooled together. No calcareous soils were included in their report.

As extraction procedures have changed over time, the early solutions used to determine the availability of more than one nutrient element (Dyer, 1894; Morgan, 1941) were replaced by those more optimally tuned to evaluate soil P availability alone (Bray & Kurtz, 1945; Olsen et al., 1954). These changes were accompanied by appropriate research in correlation and calibration. More recently the wheel has turned again, and soil test laboratories attempting to be more cost effective have pressed for procedures to determine multiple nutrient element availability (Mehlich, 1978b; Soltanpour & Schwab, 1977; Eik & Hanway, 1986). This latest shift has not always been accompanied by the requisite correlation and calibration research; rather the P recovered in the new extractant was correlated with that of the old procedure used by the lab using several samples often taken from the general pool of samples arriving at the soil testing laboratory each day. The regression equation so developed is then used to determine new criterion for fertilizer P recommendation. This approach, which reduces or eliminates the difficult correlation/calibration step in fertilizer P recommendation development, has its faults (see section IV, "Correlation of Phosphorus Soil Tests.")

D. Other Chemical Approaches to Available Soil Phosphorus Evaluation

The chemical extractants discussed previously are better related to the soil P quantity and buffer capacity factors than to soil P intensity; the P found in the soil solution. Solution phase P is determined using water or dilute salt solutions (Kamprath & Watson, 1980; Luscombe et al., 1979). Solution P concentrations are often low and dedication to analytical technique is required. Still, soil solution P is well related to plant P nutritional status. Other factors do influence the solution P level associated with P nutritional adequacy. Most notable are soil texture; sandy soils will require a higher solution P concentration for adequacy (Olsen & Watanabe, 1963); mineralogy of the clay colloid fraction (Uehara & Gillman, 1981) and the plant species being evaluated (Fox et al., 1974).

Kovar and Barber (1988) advocated several additions of P to moistened portions of each sample to predict the effect of added P on both solution P (P intensity) and the P subsequently desorbed using an anion exchange resin (P quantity). This results in a site-specific Q/I curve from each sample. McLean et al. (1982) proposed a similar procedure where only extractable P (P quantity) was determined. As the proposed equilibration period was short (2 h), a correction for the longer fertilizer-soil reaction time found in

the field was used (McLean, 1985). Lee and Bartlett (1977) used a similar technique to arrive at the Phosphorus Fertilizer Index on each sample.

Menon et al. (1989) impregnated paper strips with iron hydroxide and used those strips to desorb P from soil samples in suspension for 16 h. Phosphorus sorbed to the strips was removed by H_2SO_4 extraction. Available P test values were better related to greenhouse culture corn dry matter yield and P uptake than those of Bray P_1 , Bray P_2 , Mehlich I, Olsen, water, and resin extraction. Van der Zee et al. (1987) have described the kinetics of the strip extraction.

E. Modeling the Plant Availability of Soil Phosphorus

Another approach to available P assessment is to model the release of soluble P from other forms of residual soil P. Barrow (1980b) outlined several mechanisms behind this phenomena and summarized the information in terms of a descriptive model that simulates the initially rapid, but ultimately slow, gradual decline in available P after fertilizer addition while taking into account P removal by the harvested crop. This model, and a seemingly more mechanistic model proposed by Wolf et al. (1987), do not require a measurement of plant available P by soil test methods. They rely more upon crop response and a crop P budget developed on both fertilized and unfertilized soil, as well as previously determined empirical constants, to describe the soil transformation(s) of applied soluble P. Other models rely on soil test P information (Cox et al., 1981; Jones et al., 1984a; Sharpley et al., 1984) for initialization or evaluation.

Models that rely on crop response to residual P suffer for lack of sufficient long-term field trials with information on both P uptake and soil P transformations (Janssen et al., 1987). Models that use extractable P can be tested using successive cropping in the greenhouse to exhaust extractable P as an alternative approach to field evaluation. This has been criticized by several researchers because plants often remove more P than the decline in extractable soil P would indicate in such greenhouse trials (Novais & Kamprath, 1978; Cox et al., 1981; Adepoju et al., 1982; Fixen & Ludwick, 1982; Aquino & Hanson, 1984). This has also been observed on occasion in the field environment when the unfertilized crop yield and, therefore, plant-available P, continued to decline, but the extractable P value had levelled off (Hooker et al., 1983).

Barrow (1980b) indicated that there was a need to determine the relevant soil properties that cause differences among soils in the release of residual P. Greenhouse exhaustion trials can be used effectively to this end (Novais & Kamprath, 1978; Adepoju et al., 1982; Fixen & Ludwick, 1982; Holford, 1982; Aquino & Hanson, 1984). Properties such as clay content, pH, carbonate content, hydrous oxide content, and soluble Ca have been proposed to be related to P removal in one or more of these studies. The P cycling model of Jones et al. (1984a) makes use of several soil physical and chemical properties in predicting the residuality of fertilizer P (Sharpley et al., 1984). Cox and Lins (1984) have proposed that clay content be included in fertiliz-

er rate recommendation equations, based on the model of Cox et al. (1981), and strengthened this proposal with additional evidence (Lins et al., 1985).

Models that seek to predict changes in extractable soil P over time (Cox et al., 1981; Jones et al., 1984a, b) to make appropriate fertilizer recommendations are subject to some of the same vagaries as those soil test procedures. Initializing values are subject to differences in choice of extraction technique and in technique execution. The model may "model" the extractant's performance, but not plant-available P. For example, Barrow (1980b) suggests that bicarbonate extractable P would decline less rapidly than actual P availability on "weakly buffered" soils. Conversely, on soils with greater buffer capacity the decline in soil test P might exceed that observed by the crop. This was reported by Hooker et al. (1983) at one location using Bray P₁ to evaluate P availability to corn.

Because of a preponderance of short-term research, information is lacking on P residuality. White (1980) pointed out that P deficiency is relatively rare in most developed countries and that continued P applications to P rich agricultural soils are both uneconomical and environmentally unsound. There is a need for more "cropping down" studies so that future P fertilizer needs for such soils could be predicted with better confidence. If models are to become more important in agronomic/environmental management (reducing reliance on conventional soil testing?) more validation work must be done. Research is needed on "between-model" comparisons as well.

IV. CORRELATION OF PHOSPHORUS SOIL TESTS

The general process of soil test correlation was discussed previously (see, chapter 4 in this book, by Dahnke and Olson). Numerous correlation studies of P soil tests have been conducted with the majority of them being greenhouse experiments.

A. Greenhouse and Field Studies

As discussed earlier, greenhouse studies are sometimes preferred because the effects of uncontrolled variables can be nearly eliminated. A few precautions, however, must be taken when P tests are being correlated in the greenhouse. Plant populations or duration of the growth period should be selected to minimize competition between adjacent roots. Excessive root competition, beyond that normally encountered under field conditions, tends to overestimate the importance of the buffer capacity factor and underestimate the importance of the intensity factor (Nye & Tinker, 1977). Thus, high root densities would unduly favor tests that correlate well with the buffer capacity. Also, care must be taken to keep root zone temperatures comparable to field conditions. Unusually high or low temperatures could differentially alter reaction kinetics of both organic and inorganic P forms, influence root activity, and bias the resulting correlations.

Field experiments can also be used in P correlation studies, however, correlation coefficients will normally be lower. A multitude of climatic interactions, cultural practice differences, plant differences, and soil factors influence P uptake and crop yield under field conditions. Field correlation studies, however, have the advantage of being conducted under the same diverse conditions under which the selected test will eventually be used.

B. Comparison of Methods

A summary of the results of correlation studies conducted on 10 soil tests is reported in Table 7-2. Numerous availability parameters and their transformations were used in these experiments. Included are crop P uptake, P concentration, "A" value, resin-P, crop yield, and relative yield. In several cases, the relationship between soil test value and the availability parameter was nonlinear, resulting in log transformations or use of polynomial functions to describe the correlation. In other studies, the authors use nonfunctional correlation techniques such as the Cate-Nelson approach (see chapter 4 in this book, by Dahnke and Olson).

A wide range in correlation coefficients was found for all the soil tests evaluated (Table 7-3). Nearly every soil test varied from no significant correlation with availability to explaining more than 90% of the variability in P availability (r^2). Resin methods appear to be the exception because the lowest r value reported was 0.69. This may indicate that the resin procedures are suitable over a broader range of soil properties than the other methods. A similar conclusion was drawn by Sibbesen (1983) after reviewing and summarizing 29 published papers where the anion exchange resin method was among the P tests used. The range in r values in Table 7-3 illustrates the importance of selecting the appropriate soil test for a given set of soils. Nearly any soil test will fail if used on inappropriate soils.

C. Relationships between Soils and Soil Tests

Several soil properties influence how well specific soil tests correlate with P availability. Some of these properties are quite predictable once the basic chemistry of the extractant-soil mixture is understood. Other properties are more subtle relative to their effects on soil test success.

The presence of carbonates in soils has often been viewed as a problem for strong acid extractants such as the Bray and Kurtz methods or the Mehlich I procedure. Several studies included in Table 7-2 show a reduction in r for the Bray P_1 test compared to the NaHCO_3 test for calcareous soils (Blanchar & Caldwell, 1964, Nesse & Grava, 1986). This reduction has generally been attributed to neutralization of the acid by CaCO_3 followed by precipitation of the fluoride by the released Ca. Thus, the extractants' potential for removing P is reduced. However, in other correlation studies the Bray P_1 and NaHCO_3 tests have performed similarly on calcareous soils in Colorado and Nebraska (Olsen et al., 1954). This suggests that properties other than total CaCO_3 content are involved in determining if the acid tests

Table 7-2. Correlation coefficients of soil test extractable P with various P-availability parameters.

Region or category	No. of observa- tions	Availability parameter	Extractant†						Reference	
			Bray P		AB- DTPA	Mehlich		Water or dilute salts		
			1	2		I	II			
										Resin
Greenhouse studies										
Nigeria										
Alfisols	30	P uptake by rice	0.38	0.35	0.33	0.26		0.21‡		Oko & Agboola, 1974
Oxisols	30	P uptake by rice	0.32	0.38	0.31	0.32		0.20‡		Oko & Agboola, 1974
Poorly drained	30	P uptake by rice	0.43	0.43	0.29	0.25		0.03‡		Oko & Agboola, 1974
Combined	90	P uptake by rice	0.37	0.22	0.32	0.27		0.03‡		Oko & Agboola, 1974
Ohio										
Native pH < 5.5	10	P uptake by alfalfa	0.98§	0.99§	0.96§					Thompson & Pratt, 1954
Native pH ≥ 5.5	8	P uptake by alfalfa	0.93§	0.81	0.81					Thompson & Pratt, 1954
Combined	18	P uptake by alfalfa	0.92	0.63	0.87					Thompson & Pratt, 1954
Pennsylvania	44	P uptake, corn	0.66					0.68¶		Baker & Hall, 1967
Colorado										
Calcareous	30#	A value, oat	0.90		0.94					Olsen et al., 1954
0-9.6% CaCO ₃	38	A value, millet	0.80		0.87			0.97‡		Olsen et al., 1954
New Jersey	10	P uptake, tomato	0.70		0.88	0.73		0.72‡		van Diest, 1963
USA & Saskatchewan	74	A value, millet	0.75		0.94			0.99‡		Olsen et al., 1954
Oregon	30	A value, sudan			0.87			0.75‡		Olsen et al., 1954
Australia	18	P uptake, wheat	0.52					0.45¶		Dalal & Hallsworth, 1976
New South Wales										
7 soil orders	30	P uptake, clover	0.77		0.92	0.46				Holford, 1980
Colorado										
0.05-8% CaCO ₃	23	P uptake from multiple crops	0.88							Bowman et al., 1978
Colorado	11	Relative yield††			0.71	0.72		0.77¶		Labhsetwar & Soltanpour 1985
Minnesota										
Noncalcareous	7	P uptake, oat	0.86		0.85			0.96‡		Blanchar & Caldwell, 1964
Calcareous	7	P uptake, oat	0.23		0.73			0.95‡		Blanchar & Cladwell, 1964
Connecticut	14‡‡	Alfalfa yield	0.90			0.91				Griffin & Lorton, 1970
New York	21	P uptake, multiple			0.65					Lathwell et al., 1958
New Zealand	5	Perennial ryegrass yield			0.72			0.92§		Luscombe et al., 1979

Table 7-3. Range in correlation coefficients reported across studies for the common P soil tests.

Soil test	Correlation coefficient†	
	Minimum	Maximum
Bray P ₁	0.13	0.98
Olsen	0.03	0.96
Mehlich I	0.25	0.91
Water or salts	0.03	0.99
Resin	0.69	0.98

† Selected from Table 7-2.

fail. Because these other factors have not been completely identified, use of the acid tests is usually avoided on calcareous soils. Widening the soil to solution ratio to 1:50 or 1:100 has improved correlations on neutral and calcareous soils and apparently lessens the problem (Blanchar & Caldwell, 1964; Randall & Grava, 1971; Fixen & Carson, 1978).

The pH of noncalcareous soils has been identified as another factor influencing soil test performance, although not consistently. A field study in British Columbia showed that correlations were higher for alkaline soils than acid soils for both Bray P₁ and NaHCO₃ tests (John et al., 1967). A South Dakota study showed that correlations were lowest in the pH range of 6.6 to 7.0 for both tests (Fixen & Carson, 1978). An Ohio study demonstrated only slight reductions in correlations when the pH exceeded 5.5 for Bray P₁ and NaHCO₃ tests (Thompson & Pratt, 1954).

Holford (1980) demonstrated that P buffer capacity had a marked effect on how well Bray P₁ and NaHCO₃ soil tests correlated with P uptake. Both tests were highly correlated with uptake from weakly and moderately buffered soils ($r = 0.84-0.95$) but were not correlated with P uptake from strongly buffered soils. The author indicated that this lack of correlation may mean that a mechanism other than adsorption was dominant in buffering some of these soils.

The combined effects of carbonate content, pH, buffer capacity, and other factors on correlation coefficients can be readily observed by comparing correlations between soil series. In a Wisconsin study, the correlation coefficient for both SrCl₂ extractable P and Bray P₁ varied considerably across soil series and when the series were combined correlations dropped markedly (Table 7-4). Grouping the 90 soils by previous crop significantly increased correlation coefficients for the SrCl₂ test. Also, the soil with the lowest correlation coefficient, the Withee, was the only series with a significant mix of previous crops. Thus, cropping history may be another factor influencing correlations and perhaps P uptake.

D. Correlation between Methods

An approach commonly used when considering a new soil test procedure is to correlate the results of the standard test with the new or alternate test. Results of such comparisons are summarized for Bray P₁ and NaHCO₃

Table 7-4. Simple correlations coefficients for soil test vs. P uptake correlations (Wendt & Corey, 1981).

Soil†	Observations	Correlation coefficient	
		SrCl ₂ -P	Bray P ₁
Plainfield S	19	0.93**	0.86**
Plano Sil	15	0.98**	0.87**
Fayette Sil	15	0.85**	0.91**
Withee Sil	18	0.41	0.49*
Kewaunee Sicl and Hibbing Sicl	18	0.86**	0.71**
Total soils	90	0.43**	0.13
Previous crop:			
Row crop	50	0.81**	--
Alfalfa	40	0.64**	--

*, ** $P = 0.05$ and 0.01 , respectively.

† S, sand; Sil, silt loam; Sicl, silty clay loam.

procedures in Table 7-5. The correlation coefficients are generally high, but variation does occur in slopes and intercepts between the same procedures.

Correlation of the results from two extractants is a useful first-step technique in evaluating a new procedure. These studies can be done quickly on many soils and are relatively inexpensive. However, the results need to be interpreted cautiously. Table 7-6 shows the possible correlation coefficients between Y (yield) and Z (new soil test) given correlation coefficients between X (standard soil test) and Y and between X and Z. This table shows that as the X-Z correlation coefficients decrease, the possible range in Y-Z correlation coefficients increases rapidly and the correlations quickly become totally unreliable.

Table 7-7 demonstrates an additional concern. Examination of correlation slopes for individual soils as opposed to that for the group of individual samples indicates that the Mehlich III procedure extracts less P than Bray P₁ on the Maury soil, nearly the same on the Trappist, more on the Newark and the group of lab samples, and a great deal more than Bray P₁ on the Belknap. Without further correlation and calibration research, equivalent fertilizer P recommendations based upon the equation for the large group of lab samples would result in overfertilization of Maury (fine, mixed, mesic Typic Paleudalfs) and Trappist (clayey, mixed, mesic Typic Hapludults) soils and underfertilization of the Belknap series (coarse-silty, mixed, acid, mesic Aeric Fluvaquents). Producers owning such soils are not well served by such changes—and do not even know it. Further, this makes optimization of P fertilizer inputs to achieve economic/environmental goals difficult and reduces the value of soil testing as a management practice.

Correlations between soil tests can be useful in screening a new procedure. If the r value is low between the new test and the standard test (assuming the standard test is very well correlated with P uptake), it is doubtful that the new procedure will be acceptable and further evaluation is not likely justifiable. However, if the r value is high between the new and standard procedures, considering the correlation coefficients in Table 7-2, one can-

Table 7-5. Correlation of Bray P₁ and Olsen P soil tests with other methods.

Method (Y)	Region	No. of observations	pH range	r	Intercept	Slope	Reference
Bray P ₁ (X)							
Olsen	Florida	7	4.1-7.5	0.95	6.1 mg kg ⁻¹	0.13	Breland & Sierra, 1962
Olsen	Nebraska	15†	5.5-8.2	0.97	1.1 mg kg ⁻¹	0.43	Olsen et al., 1954
Olsen	Washington	46	--	0.87	12.2 mg kg ⁻¹	0.35	Kuo & Jellum, 1985
Olsen	South Dakota	165	6.0-8.0	0.95	3.9 mg kg ⁻¹	0.68	Malo & Gelderman, 1984
Olsen	North Cent. USA	91	4.3-6.8§	0.85	2.9 mg kg ⁻¹	0.30	Wolf & Baker, 1985
Olsen	MN, CCE < 7%	14	7.7-8.4	0.97	-2.7 mg kg ⁻¹	0.72	Nesse & Grava, 1986
Mehlich I	Florida	7	4.1-7.5	0.84	9.1 mg kg ⁻¹	0.44	Breland & Sierra, 1962
Mehlich I†	Missouri	5	6.2-6.9	0.33	--	--	Aquino & Hanson, 1984
Mehlich II	Missouri	5	6.2-6.9	0.91	--	--	Aquino & Hanson, 1984
Mehlich II	Illinois	191	--	0.97	--	--	T.R. Peck, 1984, personal commun.
Mehlich II	International	122	<7.2	0.97	--	--	Mehlich, 1978b
Mehlich III	North Cent. USA	91	4.3-6.8§	0.98	4.2 mg kg ⁻¹	0.87	Wolf & Baker, 1985
Mehlich III	SE USA	105	3.8-7.5	0.96	--	--	Mehlich, 1984
Mehlich III	Oklahoma	310	5.0-7.6	0.97	-16 kg ha ⁻¹	1.12	Hanlon & Johnson, 1984
Mehlich III	Oklahoma	310	5.0-7.6	0.94	-4 kg ha ⁻¹	0.21	Hanlon & Johnson, 1984
Bray P ₂ †	Missouri	5	6.2-6.9	0.37	--	--	Aquino & Hanson, 1984
SrCl ₂ †	Missouri	5	6.2-6.9	0.91	--	--	Aquino & Hanson, 1984
Water	Florida	7	4.1-7.5	0.91	0.61 mg kg ⁻¹	0.024	Breland & Sierra, 1962
Olsen							
Mehlich I	Florida	7	4.1-7.5	0.82	-4.1 mg kg ⁻¹	3.0	Breland & Sierra, 1962
Mehlich I	North Cent. USA	91	4.3-6.8§	0.93	0.62 mg kg ⁻¹	1.52	Wolf & Baker, 1985
Mehlich II	International	122	<7.2	0.89	--	--	Mehlich, 1978b
Mehlich III	North Cent. USA	91	4.3-6.8§	0.88	-6.91 mg kg ⁻¹	3.08	Wolf & Baker, 1985
AB-DTPA	Colorado	481	7.0-9.2	0.92	-0.63 mg kg ⁻¹	0.51	Soltanpour & Schwab, 1977
AB-DTPA	Colorado	11	6.4-7.8	0.98	-2.4 mg kg ⁻¹	0.54	Labsetwar & Soltanpour, 1985
EDTA	Colorado	11	6.4-7.8	0.91	-0.75 mg kg ⁻¹	3.0	Labsetwar & Soltanpour, 1985
EDTA	India	20	5.5-8.7	0.90	--	--	Sahrawat, 1977
CaCl ₂	Colorado	11	6.4-7.8	0.91	0.020 mg kg ⁻¹	0.027	Labsetwar & Soltanpour, 1985
log CaCl ₂	Scotland	40	5.0-6.4	0.68	--	--	Williams, 1966
Water	Florida	7	4.1-7.5	0.85	-0.0080 mg kg ⁻¹	0.16	Breland & Sierra, 1962
Log water	Scotland	40	5.0-6.4	0.66	--	--	Williams, 1966

† Slope of regression lines of extractable P vs. P removal in greenhouse study. § pH measured in 0.01 M CaCl₂.

‡ Series means used to calculate r; No. of locations = 80.

Table 7-6. Range in possible correlation coefficients between y and z calculated from given correlation coefficients between x and z (Schulte & Hodgson, 1987).

Simple correlation		Range in correlation between test 2(y) & yield (z)
(x) Test 1*(z) yield	(x)Test 1*(y) Test 2	
0.95	0.98	0.87-0.99
	0.95	0.81-0.99
	0.90	0.72-0.99
	0.85	0.64-0.97
	0.80	0.57-0.95
0.90	0.98	0.80-0.97
	0.95	0.72-0.99
	0.90	0.62-0.99
	0.85	0.54-0.99
	0.80	0.46-0.98
0.85	0.98	0.73-0.94
	0.95	0.64-0.97
	0.90	0.54-0.99
	0.85	0.44-1.00
	0.80	0.36-1.00
0.80	0.98	0.66-0.90
	0.95	0.57-0.95
	0.90	0.46-0.98
	0.85	0.36-1.00
	0.80	0.28-1.00

Table 7-7. Correlation between Mehlich III (y) and Bray P₁ (x) extractable P for individual experimental field research sites (Thom, 1985; J.H. Grove, 1987, unpublished data) and many individual soil samples received by the Univ. of Kentucky Soil Test Laboratory.

Sample group	No. of observations	M(III) vs. Bray P ₁	r
<u>Individual sites</u>			
Maury silt loam	36	y = 0.90x - 4.0	0.996
Trappist silt loam	56	y = 0.94x + 1.0	0.979
Newark silt loam	18	y = 1.29x + 9.3	0.990
Belknap silt loam	160	y = 1.43x + 3.9	0.978
<u>Individual samples</u>			
Soil test lab	510	y = 1.23x - 1.1	0.959

not predict how well correlated the new procedure will be with P uptake. Correlations between soil tests can, in some cases, be used to eliminate alternate P procedures but rarely should be used to accept new procedures. It is easy to appreciate the importance of maintaining soil sample collections for which plant P availability parameters are known.

V. CALIBRATION AND INTERPRETATION

General aspects of calibration and interpretation are covered in chapter 4 of this book by Dahnke and Olson. Factors more specific to soil test P

calibration and interpretation will be discussed here. Calibration begins subsequent to correlation of the desired soil test procedure with plant P uptake, dry matter production (yield), crop quality, or other factors of interest.

A. Soil Test Phosphorus Calibration

Calibration of a soil test P procedure involves giving meaning to a numerical extractable P value in terms of soil P availability and the likelihood of crop response to fertilizer P additions. The extractable soil P level is only one of several factors influencing plant response to P fertilizer. If all other factors are held constant, an excellent relationship between soil test P and relative yield will be obtained. Easily done in the greenhouse; this often means one location of one soil series for 1 yr in field research.

Factors complicating calibration may or may not be under control of the manager. Tillage systems can influence the soil test P level thought critical for crop response. Fixen et al. (1987) reported adequate P nutrition to corn at lower soil test P levels for no-tillage than moldboard plowed systems. It is not yet clear whether the surface stratification of P associated with no-tillage or shallow surface tillage sufficiently reduces soil P contact to influence P availability. The presence/distribution of moisture conserving residues probably plays a key role in such effects. The current literature is not consistent, but some have concluded that shallow surface soil samples are adequate to characterize P availability in such systems (Touchton et al., 1982). Surface accumulation of P was less dramatic and less likely to result in greater uptake than was that for K in another report (Blevins et al., 1986) comparing no-tillage and moldboard plowing.

Mineralization of organic P may complicate soil test P calibration. Whether driven by differences in amount and quality of organic matter, tillage system (Vivekanandan & Fixen, 1988), or liming (Lathwell, 1979), organic P release may be involved in cases where little or no crop response to fertilizer P at low soil test P values has been found (Havlin et al., 1984).

Climate, especially moisture availability, can introduce variability in crop response to available P at a single location when several years of information are combined (Randall et al., 1986; Thom, 1985) for calibration purposes. Phosphorus acquisition is strongly related to soil moisture, temperature, and texture because the nutrient is largely immobile; moving to the root surface via diffusion in water films on particle surfaces.

The largest factor complicating the calibration process is differences in soils themselves. In practice, correlation work often results in a compromise. The soil test procedure chosen works reasonably well on most soils in the area for which the test will be used by the testing laboratory. Diverse soil physiographic regions are often present. The procedure does not always work on all soils (Varvel et al., 1981) and calibration often begins by first dividing soils into different groups (response categories) *prior* to determining the level(s) of extractable P critical to P availability. Combining as few as two soils often means that the calibration loses precision to accommodate modest differences in the crop-soil P response relationship (Randall et al., 1986).

Soil properties used in prerecommendation grouping are those related to either soil P quantity or soil P buffer capacity (Holford, 1980, 1982), especially texture or the quantity of active Fe and Al (Lins et al., 1985; Bahl & Singh, 1986). Soil clay content also influences soil P availability in calcareous soils, where the solubility of Ca-P compounds is thought important to P release (Olsen et al., 1983; Fixen & Ludwick, 1982).

Correlation methodology may confuse the calibration step. Should the single large initial P application needed on some soils be included in the calibration? Rather, should calibration be based on subsequent P availability behavior that is generally similar to that of other well-fertilized soils (Lathwell, 1979; Engelstad & Terman, 1980; Uehara & Gillman, 1981)? Some investigators include but 1 yr of correlation information (Peaslee, 1978), which precludes an evaluation of the hysteresis in soil test P as cropping continues and P fertilization ceases. Soil test P has been found to fall more rapidly per unit of P removed in soybean [*Glycine max* (L.) Merr.] grain than it rose per unit of fertilizer P applied (Thom, 1985).

Ultimately, calibration results in soil test values or ranges that predict crop response to P. Phosphorus soil tests are best at predicting the probability of P response, poorer at predicting the magnitude of any response, and weakest at determining the exact rate of fertilizer P needed for optimum economic performance in any given year or field. This outcome has resulted in many approaches to the conversion of extractable soil P values into P fertilizer rate recommendations. There is a degree of uncertainty and subjectiveness to all. In chapter 4, Dahnke and Olson discuss two calibration procedures, one involving continuous functions (Mitscherlich, quadratic, and logarithmic), the other discontinuous functions (Cate-Nelson, linear plateau). Both approaches result in only a single unambiguous P critical level. Arbitrary ranges corresponding to low, medium, and high P availability can and often are superimposed on these models, however. Sanchez (1976) also thoroughly reviews the topic.

B. Soil Tests as Relative Values

The use of class intervals like low, medium, and high is usually guided by crop response, fertilizer use economics, a practical sense of farm fertilizer use rates, and the vagaries of acquiring a representative sample. Some have advocated "index" systems; a series of discontinuous functions whose discontinuities occur at intervals corresponding to low, medium, etc. (Cope, 1973), or a continuous function akin to the Mitscherlich function in shape (Hatfield, 1972; Fisher, 1974). Use of the Mitscherlich function to describe growth response to immobile nutrients has been discussed by Melsted and Peck (1973).

Another development, the "boundary line approach" has recently been proposed (Evanylo & Sumner, 1987). A scatter diagram relating yield to a soil test nutrient level is developed and lines are drawn at the boundary of the scatter. This diagram tends to illuminate peak yield regions where nutrient availability is apparently optimal. Inspection of several of the diagrams con-

tained in the Evanylo and Sumner paper (1987) suggests that a statistical approach defining the boundaries (and excluding outliers) would be useful and more suggestive of an actual response surface.

Further refinement of the yield \times soil test nutrient populations to take "nutrient balance" into account was attempted by Evanylo et al. (1987). This was an extension of Diagnosis and Recommendation Integrated System (DRIS) methodology from plant tissue nutrient composition to available soil nutrient loading. The norms (developed for soybean on highly weathered soils) were not totally successful and the authors concluded that soil nutrient balance was not critical to soybean yield determination on these soils.

Evanylo and Sumner (1987) decry the general lack of information regarding nutrient optimization from factorial-type experiments, and suggest that the optimal level derived from single factor experiments is a characteristic of the basal availability of other nutrients. Factorial experimentation is useful but logistically cumbersome. Silva (1981) has compiled several alternative designs that provide a good deal more information on nutrient interactions than single factor trials without the resource demands of full-factorial designs.

C. Soil Test Phosphorus Interpretation/Recommendation

The final step, development of a P fertilizer rate recommendation, considers several factors in addition to the previously developed calibration relationship. First and foremost, a philosophical choice must be made. Is the soil or the crop to be fertilized? The former is often described as build-up and maintenance, correction and maintenance, or simple insurance of adequacy of soil P nutrition. The latter (fertilizing the crop) is termed *sufficiency level*, sufficient level of available nutrients (SLAN), or merely the sufficiency approach.

The correction and maintenance approach presumes that high levels of P nutrition should be maintained to maximize potential gain of all crops to be grown in the field. Once such high levels are reached, soil P availability is maintained by correcting for P removal as well as P fixation. This approach conserves soil P reserves for future generations, albeit at a high level of P availability. In practice, this approach is most economical on soils with little tendency to irretrievably fix applied P and are, therefore, corrected and maintained with modest rates of fertilizer P. If regular soil sampling is done, and nutrient removal monitored, this becomes part of a nutrient "log" for a given field. This approach does tend to minimize any potential adverse effects from the occasional unrepresentative sample as well as the uncertainty of P soil test interpretation in the gray area of medium P availability.

The sufficiency approach is based upon the need of the current crop, with some common sense consideration of other components of the crop rotation under use in the field. This approach emphasizes enhanced soil P solubility at the time of greatest crop demand rather than season-long P availability. It is generally used in conjunction with P fertilizer placement to further reduce soil P interaction and fixation. There is often a slow adjustment of the soil test P level to the optimum because the sufficiency concept

recognizes the soil's competitive sinks for applied P at low soil test P levels. That optimum level is often in the medium range because of the interval between soil samples and the generally conservative nature of the approach.

Maintaining crop yield levels using sufficiency criterion and low to medium soil test P levels are well documented. Hooker et al. (1983) found that corn yields were maintained near the maximum by an annual application of 20 kg of P/ha and an average Bray P_1 value of 7 and 12 mg of P/kg on two soils for 20 and 12 yr, respectively. Touchton et al. (1982) observed that 32 kg of P/ha per yr was sufficient for wheat and double-cropped soybean each year for 3 yr. Soil test P levels were low to medium (Mehlich I extraction) at this rate. Whitney et al. (1985) examined the relationship between corn or soybean yield response and soil P (Mehlich I extraction) in Alabama and concluded little response was to be found at medium test levels. Cope (1981), reporting on 50 yr of response of five crops at six locations, determined that low to medium P availability was adequate for all these crops. In Nebraska, Olson et al. (1982) conducted a direct comparison of fertilizer recommendations from several laboratories differing in philosophy. Though surface soil P increased sharply at several locations receiving correction and maintenance P applications (as well as those of other nutrients), corn yields were not improved over those garnered with the more conservative sufficiency approach where P availability was maintained at medium levels.

The sufficiency approach is most appropriate when cash flow is limited and land tenure questionable. Environmental concerns must also be considered. Maintaining excessive soil P availability may contribute to surface water quality degradation should runoff or erosion occur.

The sufficiency approach requires more refinement and fertilizer recommendations based on this approach must consider additional factors. Some of these include differences in P source solubility, crop species, and differences in subsoil P availability among soils. Englestad and Terman (1980) ascribe differences in crop response because of fertilizer P source solubility primarily to differences in early growth of the crop in question. When the growing season is limiting such early growth, differences may be more important. Smyth and Sanchez (1982) found that rock phosphate was not able to provide adequate P for soybean on an Oxisol. Annual banded superphosphate applications were required as well.

Crop species are well known to vary in their fertilizer P response on the same soil. This observation takes on more significance when the sufficiency approach to fertilizer P recommendations is being used. Ozane (1980) has summarized several mechanisms behind such observations. In general, most research suggests that crop P requirement increases in the order: soybean [*Glycine max* (L.) merr.] < grain sorghum [*Sorghum vulgare* (L.) Pers.] = corn [*Zea mays* (L.)] < alfalfa [*Medicago sativa* (L.)] < wheat [*Triticum aestivum* (L.)]. Oat [*Avena sativa* (L.)] and clover (*Triticum* sp.) vary quite widely in this series, depending upon the observer (deMooy et al., 1973; Peaslee, 1978; Hanway & Olson, 1980). Lathwell (1979) and Uehara and Gillman (1981) have summarized similar observations on more highly weathered soils.

Subsoil P status can influence crop P fertilization requirement. Plant uptake of subsoil P has been demonstrated (Murdock & Englebert, 1958; Pothulari et al., 1986). Differences in subsoil P availability have been observed, even mapped, in some states (Hanway & Olson, 1980; Schulte, 1986).

The P fertilizer rate recommendation for a field must be based on local correlation and calibration information for soils, crops, and cultural practices appropriate to the region. Specific interpretation and recommendation information is too voluminous for a general treatise of this nature. Such material can be obtained from soils research and extension personnel at most State agricultural experiment stations and extension services.

VI. OUTLOOK

Large sample numbers in some laboratories and the development of analytical techniques (e.g., flow injection or continuous flow analysis, ion chromatography, and plasma emission spectrometry) continue to create great interest in universal extractants as discussed earlier. Caution must be exercised to avoid sacrificing the predictive ability of a procedure to expedite laboratory operations. Likewise, we must be careful not to reject improved procedures that have greater predictive ability because they are awkward in a lab's existing operation.

Stewart and Sharpley (1987) recently wrote "The limitations of present soil test methods for P and S are that they only measure inorganic forms in the soil and do not properly account for the contribution from mineralization of organic forms and past management histories. . . The challenge to soil science is to develop a complete understanding of P and S cycles in the soil for the development of more firmly based predictive relationships." As cultural systems such as tillage and rotations become more diverse, this limitation will become more critical and must be addressed.

Since 1960, limited progress has been made in how we interpret P soil tests. However, during this period we have learned much about the soil P cycle, ion transport to roots, and mechanisms of plant uptake. The challenge for soil testing in the future will be to integrate this new knowledge into our interpretation programs. The demands placed on soil P testing and interpretations will be much greater in the future than they have been in the past. This demand will include precise supplemental P requirement predictions for economic and environmental reasons as well as increased demands for P testing for waste disposal guidelines in highly populated areas. Research must continue on improved procedures and more sophisticated interpretation if these demands are to be met.

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Chapter 8

Testing Soils for Potassium, Calcium, and Magnesium¹

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High-yielding crops may contain quantities of K in excess of the amount of N. Potassium content in the aboveground portion of most forage, grain, oil, fruit, vegetable, and specialty crops ranges from a low of 40 to 50 kg of K ha⁻¹ in flax (*Linum usitatissimum*) to more than 500 kg of K ha⁻¹ in alfalfa (*Medicago sativa* L.), napiergrass (*Pennisetum purpureum* Schumach.), table beet (*Beta vulgaris* L.), and pineapple [*Ananas comosus* (L.) Merr.]. Banana crops (*Musa paradisiacac* L. var. *sapightum*) may contain 1400 kg of K ha⁻¹ in aboveground plant parts. Most commercial crops, at near-maximum economic yield, contain 100 to 300 kg of K ha⁻¹ in aerial parts. Generally, crop roots have proportionately equivalent requirements. When total crop demand is considered, soils must supply large quantities of K for plant uptake during rapid growth. The rate of K accumulation normally exceeds that of dry matter accumulation. This fact further stresses the soil's capacity to supply adequate K during certain stages of plant growth.

Crop plant Ca content will normally be less than one-half as much as K. Deficiencies of Ca as a nutrient are uncommon. Neutral and alkaline soils normally contain adequate Ca, while acid soils are usually limed to provide a favorable pH for most crops. Crops with unusually high requirements for Ca (e.g., alfalfa and peanut, *Arachis hypogaea* L.), may require more Ca or specialized Ca management to produce top yields. Magnesium content may be only one-half or less as much as Ca. Magnesium deficiencies have been reported with increasing frequency in recent years. Magnesium deficiency in livestock (hypomagnesaemia, commonly known as grass tetany)

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can occur if forages are deficient in Mg or contain an imbalance of Mg with other cation nutrients.

Generalized areas of K-, Ca-, and Mg-responsive soils in the USA and Canada are mapped in Fig. 8-1 and 8-2. These maps, based on responses to a survey of public laboratories and on the literature (Whitney, 1975; Dumanski et al., 1982; Pearen, 1984; Henry, 1985; Mahler et al., 1985; Penney, 1985), reflect both the experience and the philosophy of soil-testing laboratory directors. They have been drawn to correspond in general with major soil boundaries and agricultural areas. However, divisions between areas of responsive and nonresponsive soils sometimes are arbitrary; that is, they may follow political boundaries, rather than recognized changes in soil characteristics.

There are instances of crop response to fertilizer K, Ca, and Mg that cannot be predicted from soil characteristics alone. For example, small grain responses to fertilizer K are highly dependent on seasonal weather conditions in Montana. This is due partly to soil water and temperature influences on

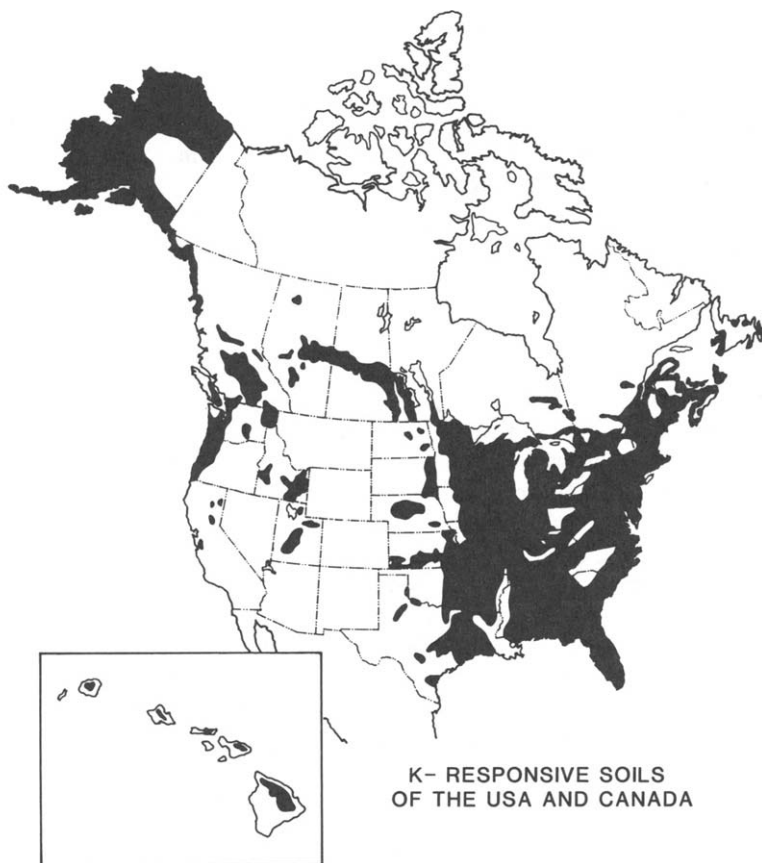


Fig. 8-1. Generalized areas of soil in the USA and Canada on which crops frequently respond to K applications (from a survey of public soil-testing laboratories conducted by Russelle). See text for further details.

the rate of K diffusion to plant roots (Schaff & Skogley, 1982a; Skogley & Schaff, 1985). Potassium deficiency in cotton (*Gossypium hirsutum* L.) has been induced by disease (Ashworth et al., 1982). It is difficult to separate the effect of Ca from the liming effect. Calcium is usually supplied as calcitic or dolomitic limestone to acid, potentially Ca-deficient soils. In the arid West, Ca responses are often found on soils of high Na content (e.g., in Alberta and California). Magnesium deficiencies can be due to high K/Mg ratios in soils (e.g., in Nevada), rather than to a lack of Mg per se.

Crops grown on sandy soils in many parts of North America frequently will respond to applications of K, Ca, and Mg, particularly under irrigated conditions. Crops also have significantly different requirements for these elements. A soil may have insufficient K supply for alfalfa, but maximum corn (*Zea mays* L.) grain yields may be achieved without additional K. Under these conditions, consider Fig. 8-1 and 8-2 *highly* generalized. They should not be used to predict crop responses in specific situations.

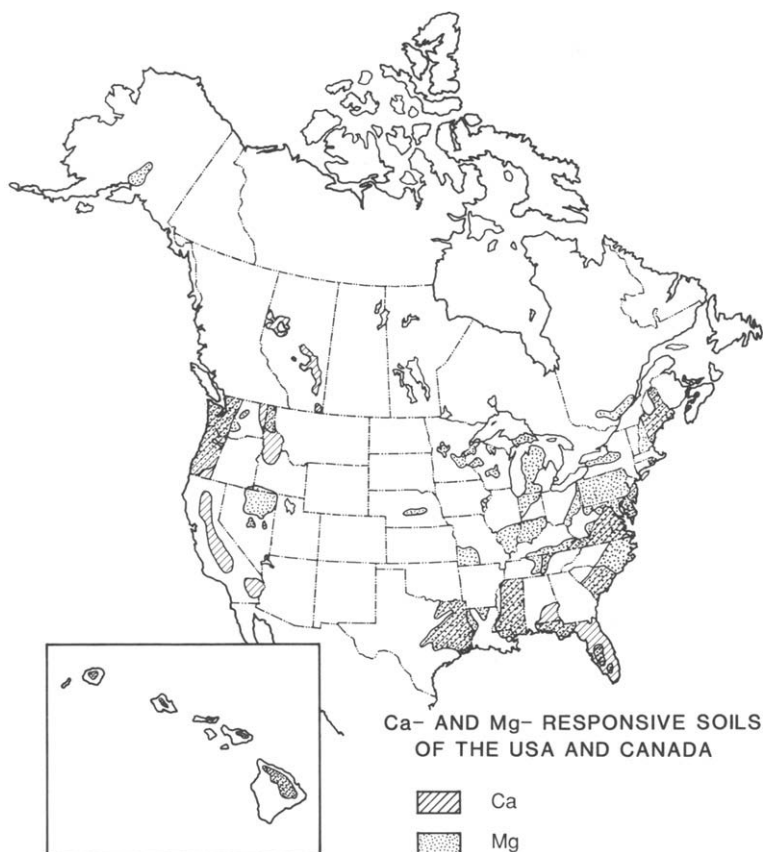


Fig. 8-2. Generalized areas of soils in the USA and Canada on which crops frequently respond to applications of Ca and Mg (from a survey of public soil-testing laboratories conducted by Russelle). See text for further details.

Analytical procedures for plant-available soil K, Ca, and Mg must provide a good relationship between test results and actual nutrient availability during the growing season for a specific crop. "Mass flow" and "diffusion" are the two processes through which nearly all of the K, Ca, and Mg ions are moved from their original position in the soil solution to the root surface where they can be taken up by the plant (see chapter 3 in this book, by James and Wells). Other equilibria and dynamic aspects of "exchangeable" or "slowly available" ions also influence true nutrient availability to crops. Nutrient extraction procedures that do not directly account for these soil processes and for the influence of soil, site, and weather conditions on each process will, at best, be estimates or indexes of nutrient availability. However, it is necessary that analytical procedures be simple and rapid. They are useful tests if the extracted nutrients relate closely to the amounts of K, Ca, and Mg that actually become available to plants during the growing season. The extreme range of soil, crop, and growing conditions for which tests are used dictates that no one approach will likely be successful for all situations. Procedures selected for use in a specific location are generally those that have provided the best correlation to K, Ca, and Mg availability for specified crops of that area.

I. MINERALOGY, EQUILIBRIA, AND DYNAMICS THAT MAY AFFECT SOIL TEST RESULTS

A. Potassium

Soil K has been categorized into soluble, exchangeable, fixed, and structural K (Sparks & Huang, 1985). The interrelations among these forms of soil K are illustrated in Fig. 8-3. Procedures that are based on extractable

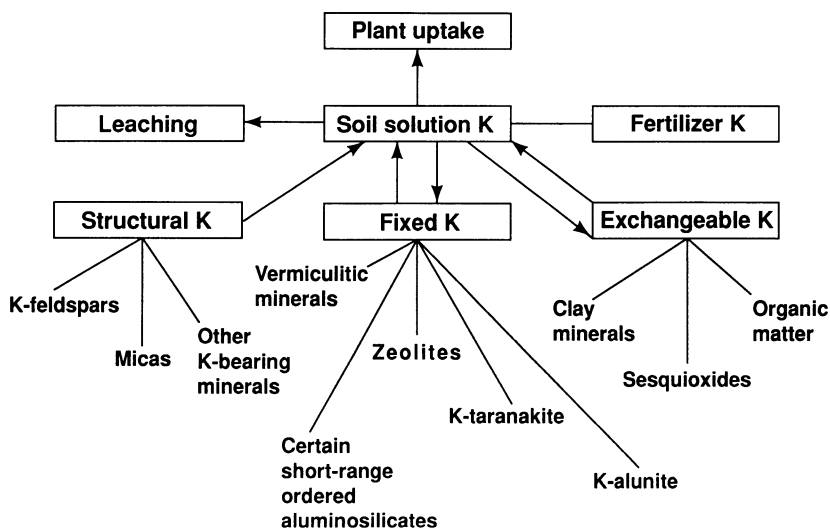


Fig. 8-3. Interrelationship of various forms of soil K (Sparks & Huang, 1985).

K measure soil solution K^+ , most of the exchangeable K, and small, but varying, proportions of fixed or structural K. Numerous processes regulate the dynamics of the soil-K-plant system. Measurement of extractable K from a soil sample treated in a specific manner can be expected to serve only as an index to plant-available K.

The direction and rate of equilibrium reactions in the soil largely determine the fate of applied K. Added K can be taken up by plants, maintained in available forms in the soil, converted to less available forms, or leached to lower horizons. More precise fertilizer management recommendations could be made if the various reaction parameters were known for these processes in any given soil. The complexity of the system across different soils makes this a difficult area of research. However, based on results of research with many different soils and a wide range of conditions, it is possible to provide a generalized expression of reaction rates for the possible inter-conversions among the four major forms of soil K (Table 8-1). Recent detailed reviews of these aspects of soil K availability have been presented by Bertsch and Thomas (1985) and Sparks and Huang (1985).

The following discussion is presented as a general review of the soil-K plant system. It is intended to serve as a basis for understanding the different approaches used in testing soils for K and to help realize the strengths and limitations of various analytical methods.

1. Structural Potassium

The original source of K in soils is from weathering of rocks containing K-bearing minerals. Feldspars and micas are considered to be most important in this regard (Tisdale et al., 1985). The generalized chemical composition and approximate K content of important K-bearing feldspar and mica minerals are presented in Table 8-2.

When primary minerals are physically and chemically altered, secondary layer silicate clays may be formed. These can have K present in the crystal structure or in interlayer positions. Such minerals (e.g., dioctahedral or trioctahedral illite) can influence the supply and availability of K^+ to plants, depending on amounts present, degree of weathering, and past soil management.

2. Potassium on Clay Minerals and Organic Matter

Soil clays and organic matter influence K^+ availability in several ways. Exchange sites of clay minerals attract K^+ , providing a sink of readily

Table 8-1. Generalized rate of reaction for conversion of soil K from one form to another (see Fig. 8-3).

Soil K form	Rate of conversion to soil solution K^+ †
Structural K (feldspars, micas, etc.)	Slow, geological process (yr)
Fixed K^+	Several hours to several weeks
Exchangeable K^+	Nearly instantaneous to several hours

† Reverse reactions, where they can occur, would be generally similar in rate.

Table 8-2. Some important K-bearing primary minerals (based on Malavolta, 1985; and Rich, 1968).

Mineral	Chemical composition	Potassium content, g kg ⁻¹
Feldspar		110-150
Orthoclase	(K, Na)AlSi ₃ O ₈	
Microcline	(Na, K)AlSi ₃ O ₈	
Sanidine	KAlSi ₃ O ₈	
Micas		
Muscovite	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	80
Biotite	K(Mg, Fe ²⁺) ₃ (AlSi ₃)O ₁₀ (OH) ₂	70
Phlogopite	KMg ₃ (AlSi ₃)O ₁₀ (OH) ₂	70

exchangeable K in dynamic equilibrium with K⁺ in the soil solution. Because of electrical attraction, movement of K⁺ in soils by either mass flow or diffusion is not a simple process. Quantities and types of clays (McLean, 1978), soil water and temperature effects (Schaff & Skogley, 1982a), and other factors interact to create a complex situation concerning soil clays and the availability of K⁺ to plants.

Three types of adsorption sites for K on clay minerals have been postulated (Fig. 8-4). Those on planar surfaces (p-position) have low K⁺ selectivity, those on edges (e-position) have medium K⁺ selectivity, and those in interlayer sites (i-position) have high K⁺ selectivity. The K present in the i-position is referred to as "fixed" K. Fixed K adds an additional dimension to plant-K availability due to slow rates of release. Micaceous-, illitic-, and smectitic-clays (in decreasing order of K in i-positions) are involved in this relationship. Soils that contain a large proportion of these clays will exhibit varying degrees of K⁺ fixation and/or release. Availability of added fertilizer K may be reduced in soils with high-fixation capacity. Under certain conditions, K⁺ from interlayer positions may contribute substantially toward meeting crop K demands (Mengel & Kirkby, 1980). Miller (1988) found that wheat (*Triticum aestivum* L.) used nonexchangeable K in the near rhizosphere over extractable and solution K at greater distances in soils containing illitic-type clays.

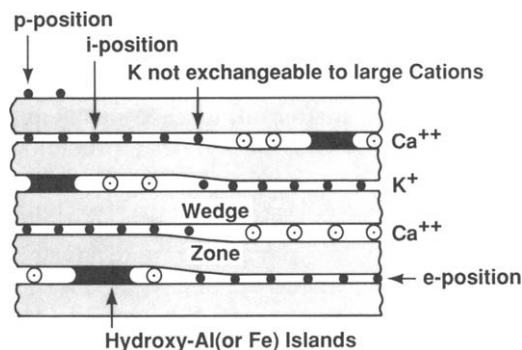


Fig. 8-4. Model of an expandable 2:1 clay mineral with interlayer K⁺, wedge zones, and p-, e-, and i-positions (Mengel & Kirkby, 1980).

Soil organic matter imparts additional complexity to the K-availability system. Acidic functional groups (carboxyls, phenols, and enols) or organic polymers are sources of negative charge in the soil. The extent of dissociation of these functional groups depends on pH, electrolyte concentration, and cation species, but the charge is high ($200\text{--}400\text{ cmol}_c\text{ kg}^{-1}$) compared to that of phyllosilicates ($1\text{--}200\text{ cmol}_c\text{ kg}^{-1}$) (Greenland & Hayes, 1978). The affinity of soil organic matter exchange sites for K^+ is relatively low (Allison, 1973) and certainly much less than when micaceous or illitic clays are involved (Mengel & Kirkby, 1980). Hence, organic matter-derived cation-exchange capacity (CEC) contributes less to soil K^+ relations than its proportionate share of the exchange complex. As a result, it is often overlooked when considering soil factors of importance in K availability. This may be a serious oversight, especially in soils containing several percent organic matter.

Clays and organic materials also form many complexes that can result in altered surface charge properties of both the clay and the organic matter (Allison, 1973). Organic polymers may also be involved in the release of fixed K as a result of their chelating powers (Tan, 1978). Consequently, additions of organic materials to soils and actions and products of roots and micro-organisms growing in the soil should not be overlooked as factors that can influence soil-K availability.

3. Soil Solution Potassium

The soil solution is the medium from which plants absorb nutrients. The concentration of K^+ in soil solution is highly important to plant-K availability. The higher the concentration, the greater will be K^+ movement toward plant roots via mass flow, and the greater will be the diffusion gradient (assuming a K^+ depletion zone surrounding absorbing roots). Other factors influence mass flow and diffusion rates. These include soil water content, temperature, and tortuosity of the diffusion path (Bertsch & Thomas, 1985). Nevertheless, K^+ concentrations and gradients develop the primary influences and driving forces for these processes.

A major problem in studying soil-solution nutrient relations has been the difficulty in separating solution and solid phases without altering the nutrient composition of the solution. Adams (1974) listed five categories of methods that have been used in attempting to obtain soil-solution samples. These are: (i) suction or pressure, (ii) displacement, (iii) compaction, (iv) centrifugation, and (v) molecular adsorption. Only the first two methods have been used to any large extent, due to serious deficiencies encountered with the latter three approaches. However, more recently the centrifugation approach has been successfully developed by using heavy organic liquids that are immiscible with water to displace soil solutions under large centrifugal forces (Mubarek & Olsen, 1976).

Most data in the literature concerning soil solution composition have been obtained from either the suction/pressure method or by displacement. Displacement in this terminology involves placing a column of water over

Table 8-3. Soil solution concentration of K^+ in ILD extracts and extractable K^+ as influenced by temperature, soil water tension (ψ), and K additions to Amsterdam silt loam, 0 to 15 cm (Skogley, 1986). Values are means for samples taken 3 and 14 d after K fertilization.

Added K kg ha ⁻¹	5°C		20°C	
	100 kPa (1 bar)	33 kPa ($\frac{1}{3}$ bar)	100 kPa (1 bar)	33 kPa ($\frac{1}{3}$ bar)
	Soil solution K^+ , mg L ⁻¹			
0	48.9	39.5	60.2	48.5
100	72.3	61.4	84.1	71.6
400	190	162	220	176
	NH_4 -OAc-Extractable, cmol _c K ⁺ kg ⁻¹			
0	1.22	1.23	1.31	1.34
100	1.50	1.51	1.51	1.55
400	2.01	2.08	2.08	2.04

a moist column of soil and collecting the desired quantity of displaced liquid at the bottom of the column. In the suction/pressure method, soils are normally wetted to levels above field-normal conditions (e.g., saturated paste extracts) to obviate problems relative to small quantities of extracts. Results from either of these types of extracts will not truly represent quantities and proportions of various ions that would exist under lower soil water contents. Consider, for example, the influence of the "ratio law" on relative concentrations of K^+ and Ca^{2+} as the soil solution becomes more dilute (Thomas, 1974). Even under field conditions, the composition of the soil solution will vary according to soil properties, soil water content, and rate of nutrient extraction by plant roots. Hence, meaningful studies based on soil-solution analysis are difficult to develop, but the nearer one can simulate conditions that exist during plant growth, the more useful the results should be. This is a major advantage of the immiscible liquid displacement (ILD) method.

A large range exists in reported values for K^+ in soil solutions. Most of the data from column displacement or pressure/vacuum extractions fall within about 1 and 265 mg of K^+ L⁻¹ for a broad selection of soils and soil conditions from various areas of the world (Nemeth et al., 1970; Adams, 1974; Barber, 1984). Most values for normal agricultural soils of humid regions fall within 2 to 5 mg of K^+ L⁻¹, whereas most from arid region soils are an order of magnitude higher. Results from a study where K^+ contents of ILD extracts from a semiarid Amsterdam silt loam (fine-silty, mixed Typic Haploboroll) were measured are summarized in Table 8-3 (Skogley, 1986). The influence of soil water content (within a range normal for field conditions), temperature, and added fertilizer K are shown, as are values for ammonium acetate-extractable K^+ . Converting these latter values to soil test ratings in mg kg⁻¹ shows that the soil was one that would test "high" in available K^+ (477-813 mg kg⁻¹) when fertilizer K was not added.

Soil-solution concentrations of K^+ from ILD extraction are at the high end of the range of soil solution K^+ values of normal arid region soils as reported by Barber (1984). This would be expected because there is no dilu-

tion of the soil solution in the ILD method. The data illustrate the wide range of values that can occur in response to soil conditions. Even within the wet end of plant-available water (33–100 kPa), the drier the soil, the higher the K^+ concentration. Warmer-extraction temperature also resulted in higher solution K^+ concentrations. Additions of fertilizer K (as KCl) dramatically increased solution K^+ . Additions in the range of normal crop K utilization (100–400 kg of K ha⁻¹) resulted in up to 4.1-fold increase in solution K^+ . Ammonium acetate-extractable K^+ increased a maximum of 1.7-fold. Ching and Barber (1979), using the column displacement method of soil-solution extraction, reported similar effects of soil temperature and added K on soil-solution K^+ concentration, although their absolute values were much lower.

Results of studies with soil solution provide evidence to help explain why specific soil test methods, based on extractable K, sometimes fail to be strongly related to true nutrient availability and uptake by crops. Extractable K is not nearly as sensitive to changes in conditions as is soil-solution K^+ . Furthermore, extractable K does not account for most processes that may become rate-limiting to K availability.

4. Equilibria and Dynamics Affecting Phytoavailability of Potassium

Thermodynamic principles have long been used to obtain exchange coefficients and thermodynamic parameters for various cation-exchange systems (e.g., Gaines & Thomas, 1953). More recently, studies have been conducted using chemical kinetic approaches to determine thermodynamic parameters for K^+ exchange in clays and soils (Sparks & Jardine, 1981; Jardine & Sparks, 1984; Barber, 1985; Sparks & Huang, 1985). Since K^+ movement to plant roots is a dynamic process, thermodynamic equilibrium of K^+ with the soil probably never occurs in the active rhizosphere during crop growth. Hence it is reasoned that evaluation of K^+ availability will be more realistic if it is based on a modelling approach in which kinetic parameters are used, rather than those based primarily on calculations of thermodynamic equilibrium (Barber, 1984).

The root-soil interfacial zone contains only a small amount of a plant's total requirement for K^+ . Root volume of annual crops is <1% of soil volume. Thus, the K requirement of the plant obtained from this zone will be small (Barber, 1985). The remainder of the K required by the crop will have to move in the soil to plant root surfaces either in the water being drawn to the root in response to transpiration (mass flow) or by diffusion. If the concentration of K^+ in the soil solution that moves by mass flow is sufficiently high, most or all of the crop K^+ demand could be met in this manner. Any deficit from this process would have to be satisfied by diffusion. Actually, both processes would normally be operating simultaneously during active crop growth. The relative importance of each in supplying K^+ will depend on soil conditions, most of which are in a continual state of change.

Estimates of the relative contribution of mass flow can be made if the total crop K uptake, water use, and soil-solution K^+ concentration are

known. Using this approach, Barber (1985) suggested that the soil-solution K^+ concentration would need to be maintained near 100 mg of K^+ L^{-1} to completely satisfy crop K demands through mass flow. Saturation paste extracts or column-extracted soil solution K^+ concentrations range from 2 to 60 mg L^{-1} . Even soil-solution extracts obtained by ILD extraction from a soil "high" in extractable K (see Table 8-3) have concentrations that account for only 30 to 40% of crop K requirements via mass flow (Skogley, 1986). Mass flow could be expected to account for most of the K^+ movement to crop roots only when relatively high rates of fertilizer K are applied to the soil and when most of the water absorbed by plant roots comes from the fertilized zone. Thus, under most cropping conditions, a large fraction of the total crop K demand would have to move to roots in response to a diffusion gradient. When diffusion is impeded for any reason (e.g., cold or dry soil conditions), it could be a rate-limiting process for K^+ availability to crops.

To understand the dynamic soil-K plant system, it is necessary to learn about related mechanisms and conditions in both the soil and the plant. Plant factors include plant age, K status, temperature, transpiration rate, root morphology and growth rate, and K^+ -absorption mechanisms of the root. Soil conditions of importance include those factors that influence K^+ diffusion (temperature, water content, tortuosity, and K^+ concentration of soil solution) and exchangeable-K relations (amounts and proportions of K to other cations, soil-K buffer capacity, rate of release to solution phase), as well as soil solution parameters and plant water use related to mass flow. Barber (1984) and his associates have developed models to predict K^+ uptake by corn and soybean [*Glycine max* (L.) Merr.] Their results suggest that root morphology and rate of growth contribute most strongly to total K uptake, followed by soil parameters that control K^+ flux in the soil. These parameters include initial K^+ concentration of the soil solution, soil K^+ buffer power, and the effective diffusion coefficient of K^+ in the soil.

B. Calcium

1. Calcium Sources

The Ca content of earth's crust averages about 36.4 g kg^{-1} . The majority of this Ca exists as difficultly soluble primary minerals. These minerals include the Ca-bearing aluminum silicates such as feldspars, amphiboles, Ca phosphates, and Ca carbonates, the latter being particularly important in calcareous soils (Mengel & Kirkby, 1978). The plagioclase mineral, anorthite ($CaAl_2Si_2O_8$), is the most important primary source of Ca (Tisdale et al., 1985). Other minerals in this group, including impure albite, are of less significance. Pyroxenes (augite) and amphiboles (hornblende) are fairly common Ca minerals in soils. Calcium may also be solubilized from biotite, epidote, apatite, and certain borosilicate minerals.

Soils vary widely in Ca content. Coarse-textured, humid-region soils formed from rocks low in Ca-containing minerals are low in Ca. Humid

region soils formed from limestones are frequently acid in the surface layers because of the removal of Ca and other basic cations by leaching. Calcium carbonate, or calcite (CaCO_3), is often the dominant source of Ca in soils of semiarid and arid regions. Dolomite [$\text{CaMg}(\text{CO}_3)_2$] may also be present in association with calcite. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is present in some soils in semiarid regions.

2. Forms of Calcium

Calcium in soils may be classified as nonexchangeable which includes mineral forms, exchangeable, and soil solution Ca^{2+} . Calcium is usually the most dominant of soil-exchangeable cations. Exchangeable Ca is the major reserve of soil Ca available to plant roots and can range from $<25 \text{ mg kg}^{-1}$ to more than 5000 mg kg^{-1} . Lower exchangeable Ca concentrations exist mainly in low CEC, acid, humid region soils. Higher Ca levels are found in higher CEC, semiarid and arid region soils that contain CaCO_3 , and in limed acid soils. The term extractable is preferred instead of exchangeable for Ca removed by dissolution of CaCO_3 from alkaline or limed acid soils by acidified extracting solutions. The advent of inductively coupled plasma emission (ICP) spectrometers allows nutrient levels to be analyzed at much higher ranges. As a result, extractable Ca levels $>45\,000 \text{ mg kg}^{-1}$ are sometimes reported.

Calcium is absorbed by plants as Ca^{2+} from soil solution. Rapid equilibrium occurs between exchangeable Ca and soil-solution Ca^{2+} . The amount of Ca^{2+} in soil solution is usually high relative to other cations in nonsodic soils. Adams and Henderson (1962) cited soil solution Ca^{2+} values ranging from 68 to 778 mg kg^{-1} from many experiments.

3. Factors Affecting Uptake

Soil factors of greatest importance that determine Ca availability to plants are listed by Tisdale et al. (1985) as total Ca supply, soil pH, CEC, Ca-saturation percentage of the soil colloids, type of soil colloid, and the ratio of Ca^{2+} to other cations in solution.

a. Calcium Supply. The CaO content of soil ranges from about 55 g kg^{-1} in Aridisols (arid region soils) to 16 g kg^{-1} in Mollisols (grassland prairie soils) and $<10 \text{ g kg}^{-1}$ in older soils such as Alfisols, Spodosols, Ultisols, and Oxisols (humid region soils) (McLean, 1975). Calcium has an ion diameter of $9.9 \times 10^{-9} \text{ cm}$ and forms a base on hydrolysis. Calcium moves to the root surface by mass flow in response to the transpiration stream, by root interception of growing roots, or by ion diffusion from higher to lower concentrations (McLean, 1975).

Calcium availability to the plant is largely a factor of the supply in the soil but can be affected by soil properties. In very sandy, acid soils with low CEC, Ca supply can be too low to provide sufficient available Ca to crops. Adams and Moore (1983) reported visual symptoms of Ca deficiency in cotton roots when the soil E and B horizon solution Ca^{2+} concentration ranged

between 10.8 and 13.6 mg kg⁻¹ and the Ca-saturation level was 170 g kg⁻¹ or less. Melsted (1953) observed Ca-deficiency symptoms in corn grown on acid soils containing < 400 mg extractable Ca kg⁻¹. He noted that Ca deficiency was not evident until all other nutrient deficiencies were corrected by large applications of soluble fertilizers. Deficiencies were verified by plant Ca concentrations of 2 g kg⁻¹ or less.

b. Soil pH. Semiarid and arid region soils are relatively unweathered. Alkaline soils of these regions usually contain an excess of Ca in the plant-rooting depth. Much of this Ca is in the form of CaCO₃ that has a solubility of about 5.6 mg Ca L⁻¹ in cold water. The majority of crops in these regions are adequately supplied with Ca. Calcium concentration of 0.25 mg L⁻¹ was sufficient to obtain maximum growth rates in a nutrient solution at pH 5.6 (Lund, 1970). More than 2.5 mg Ca²⁺ L⁻¹ was required at a solution pH of 4.5, and 5 mg of Ca²⁺ L⁻¹ was insufficient when pH was 4.0. This is in agreement with Melsted's (1953) earlier field research on pH 4.5 soils. The elongation rate of cotton roots in 0.001 M CaHPO₄ adjusted to varying pH levels with H₃PO₄ was inhibited only at solution pH < 4.25 (Howard & Adams, 1965). Soils approaching this pH level rarely remain in agronomic crop production.

c. Cation Exchange Capacity, Calcium Saturation, and Type of Soil Colloid. Cation exchange capacity is important to soil Ca availability in relation to the Ca saturation of soil colloids and the type of soil colloids. Soil CEC increases with increasing soil pH. This is notable relative to cation saturation percentages. Many crops respond to Ca applications when the degree of Ca saturation of soil CEC falls below 25%. Kaolinite clays are able to satisfy the Ca requirements of most plants at saturation values of only 40 to 50%. Soil clays with two silica to one octahedral layer (2:1), such as montmorillonite, require a Ca saturation of 70% or more before this element is released in sufficient supply to growing plants (Tisdale et al., 1985). Allaway (1945) found that the availability of the replaceable Ca from various colloids as measured by soybean uptake was in the order peat > kaolinite > illite > Wyoming bentonite > Mississippi bentonite. At 40% saturation, kaolinite supplied soybean with more Ca than did Mississippi bentonite at 80% saturation.

d. Cation Ratio. The cation-ratio concept probably originated from New Jersey work that projected an ideal soil as one with the following distribution of exchangeable cations: 65% Ca, 10% Mg, 5% K, and 20% H (Bear et al., 1945). These concentrations provide the ratios: Ca/Mg of 6.5:1, Ca/K of 13:1, and Mg/K of 2:1. Bear et al. (1945) proposed 65% as the Ca saturation of the CEC of the ideal soil for optimum plant growth. Graham (1959) suggested modification of the ideal Ca-saturation ratio to a range of 65 to 85%. Eckert and McLean (1981) reported that German millet (*Setaria italica* L. Beauv.) grew best at Ca saturations below the minimum level of 65%. Geraldson (1957) indicated that excess total salts can cause a Ca deficiency in tomato (*Lycopersicon esculentum* Mill.) even when the Ca ratio is con-

sidered high or adequate. He reported that Ca^{2+} uptake by tomato was decreased to the greatest degree by the NH_4^+ ion. Claassen and Wilcox (1974) reported a similar effect of NH_4^+ on Ca^{2+} absorption by corn.

McLean et al. (1983) found poor correlation between yield response of corn, soybean, wheat, and alfalfa to Ca/Mg ratios. The average of 83% saturation of the CEC was common for maximum and minimum yields. Soil pH was better correlated with yields than cation ratios or basic cation saturation ratio (BCSR). Eckert (1987) found that wide variations in BCSR ratios were of little consequence as long as gross imbalances were not created. He found no results in the literature that confirmed the existence of the ideal cation saturation ratio. Liebhardt (1981) also concluded that Ca and Mg recommendations based on cation saturation percentages and the resulting Ca/Mg and Ca/K ratios are not warranted. He suggested maintenance of Ca^{2+} availability to plants by use of a liming program that maintains soil pH between 5.5 and 6.0. Liming to these pH levels generally maintains the Ca + Mg saturation levels between 65 to 75%, alleviates metal toxicities, and increases availability of other fertilizer nutrients.

C. Magnesium

1. Magnesium Sources

The Mg content of most soils generally ranges between 0.5 g kg^{-1} for sandy soils and 5 g kg^{-1} for clay soils (Mengel & Kirkby, 1978). Magnesium is present in relatively easily weatherable ferromagnesian minerals such as biotite, serpentine, hornblende, and olivine. It occurs in secondary clay minerals including chlorite, vermiculite, montmorillonite, and illite. Some soils contain Mg as MgCO_3 or $\text{CaMg}(\text{CO}_3)_2$. In arid or semiarid regions, soils may contain large amounts of Mg as MgSO_4 .

2. Forms of Magnesium

Soil Mg may be divided into nonexchangeable, exchangeable, and water-soluble forms, all in equilibrium. In a fractionation study of selected temperate and tropical soils, Mokwunye and Melsted (1972) ranked Mg distribution in the following order: primary > acid soluble > exchangeable > organically complexed. Soil Mg is a moderately leachable nutrient, and as with Ca, greater amounts are often found in the subsoil than in upper parts of the profile. Highly leached and weathered soils such as Alfisols, Ultisols, and Oxisols are generally low in Mg compared to the relatively unweathered soils such as Entisols, Vertisols, Inceptisols, Aridisols, and Mollisols.

Magnesium is taken up by plants as Mg^{2+} from soil solution. Expandable clay minerals supply Mg^{2+} to plants from both lattice and interlayer positions (Christenson & Doll, 1973). Exchangeable Mg normally constitutes from 4 to 20% of the CEC (Mengel & Kirkby, 1978), and varies between

17 and 2431 mg L⁻¹ in soil solution (Fried & Shapiro, 1961). Most frequently, concentrations exist between 50 and 120 mg L⁻¹ (Mengel & Kirkby, 1978).

3. Factors Affecting Uptake

Soil factors that affect Mg²⁺ uptake by plants include Mg²⁺ supply, soil pH, K application rate, soil CEC, percent Mg saturation, soil texture, type of soil colloid, and Mg/cation ratio (Tisdale et al., 1985).

a. Magnesium Supply. The total Mg supply in the Ap layer of five southeastern USA sandy, acid Coastal Plains soils ranged from 89 to 302 mg kg⁻¹ (Rice & Kamprath, 1968). The percentage of the total Mg in exchangeable form ranged from 3.8 to 9.4 g kg⁻¹, and generally increased as total Mg increased. Prince et al. (1947) found no correlation between the total Mg in eastern USA soils and their crop-yield potential.

Plant-available Mg is largely in the exchangeable and water-soluble forms (Arnold, 1967). Fox and Piekielek (1984) reported that the exchangeable Mg level recommended for agronomic crop production by different soil-testing services ranged from 25 to 180 mg kg⁻¹. Arnold (1967) reported that soils most susceptible to Mg deficiency are light-textured, acid soils with low-exchangeable Mg levels and soils of high K status regardless of exchangeable Mg level. Reith (1967) found depressed Mg²⁺ supply to plants when K was applied in excess to soils already containing satisfactory or high K contents. A 1.2 ratio of Mg/K was reported by Hooper (1967) as the level needed to obtain a Mg concentration of 2 g kg⁻¹ in herbage. Magnesium

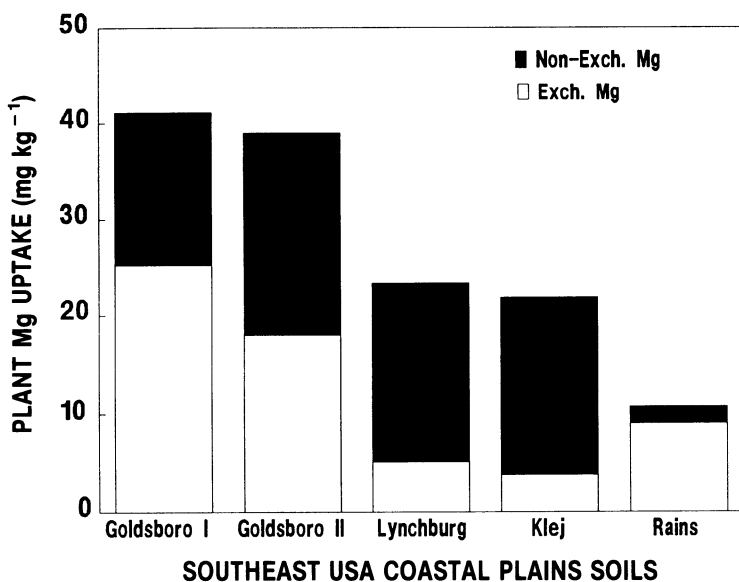


Fig. 8-5. Plant uptake of Mg from exchangeable and nonexchangeable sources. (Data from Rice & Kamprath, 1968.)

uptake was lowered by Ca^{2+} (Farina et al., 1980) and by NH_4^+ (Claassen & Wilcox, 1974).

The soil content of available Mg thought to be deficient or adequate varies. Georgia soils containing 50 mg kg^{-1} or less had inadequate Mg^{2+} for good plant growth (Boswell et al., 1967; Gallaher et al., 1975). According to Reith (1967) in northern Scotland, responses could be expected in slightly acid mineral soils at Mg^{2+} levels below 30 mg kg^{-1} when extracted by tumbling end-over-end in a 1:40 soil:2.5% acetic acid solution for 2 h. Adequate Mg levels could be attained with 160 mg kg^{-1} soluble Mg^{2+} in the soil. Haby et al. (1979) reported no response of Coastal bermudagrass to Mg application when the surface 15 cm of an Alfisol contained 7.3 mg of Mg kg^{-1} , and similar lack of corn response on another Alfisol that contained 36 mg of Mg kg^{-1} . According to Rice and Kamprath (1968), exchangeable Mg in the range of 6.1 to 28 mg kg^{-1} appeared to be equally available for plant uptake because the plants obtained a large part of their Mg from nonexchangeable forms (Fig. 8-5). Charlesworth (1967) related the Mg content of carrot (*Daucus carota* var. *sativus* [Hoffm.] Arcang.) leaves to Mg content within the upper 45 cm of soil.

b. Soil pH. The effect of soil pH on Mg availability is related to several factors. Sudangrass [*Sorghum vulgare sudanense* (Piper) Hitchc.] response to Mg was greatest at pH 6.5 on Norfolk loamy sand (fine-loamy, siliceous, thermic Typic Paleudult) and on Hartsells fine sand (fine-loamy, siliceous, thermic Typic Hapludult), but was lower at pH 6.5 than at 5.5 on the Dickson silt loam (fine-silty, siliceous, thermic Glossic Fragiudult) (Adams & Henderson, 1962). Total soil Mg tended to be less at pH 6.5 than at 5.5 on Mg-deficient soils, but was greater at pH 6.5 on Mg-sufficient soils. Christenson et al. (1973) indicated that low pH affected Mg uptake by oat (*Avena sativa* L.) only when the Mg level in the soil was low. Hooper (1967) determined that soil test correlations between several soil-extraction methods and percentage Mg in herbage were consistently greater at pH > 6.5 . Increasing pH markedly decreased 0.01 M CaCl_2 extractable Mg while double-acid Mg availability remained essentially unchanged (Farina et al., 1980). In some soils, yields were depressed by high pH levels and Mg content was lower, but Mg applications did not increase yields. Evidence suggested that salt-extractable Mg did not accurately reflect plant availability. According to Jones and Haghiri (1963), increasing pH had a greater effect on Mg^{2+} uptake, whereas the addition of Mg without an increase in soil pH had only a slight effect on uptake of Mg^{2+} .

c. Potassium Supply. Considerable evidence indicates that heavy applications of potash fertilizer or a high level of K^+ in the soil can lead to a low-Mg content in the plant. Doll and Hossner (1964) reported that fertilizer K decreased potato (*Solanum tuberosum* L.) yields at every level of Mg fertilization. Stout and Baker (1981) indicated that the differential adsorption of K was the controlling factor in the uptake of Mg by corn seedlings. Soil K was significantly correlated with Mg concentration in corn plants but explained $< 40\%$ of the variation in plant uptake of K^+ (Walker & Peck,

1975). Rahmatullah and Baker (1981) reported a correlation between Mg concentration in corn and $\frac{1}{2}$ pMg-pK, an expression of the relative availability of Mg and K by the Baker method (Baker & Amacher, 1981). Data indicated the plant uptake of Mg from these soils was more a function of K availability than of Mg availability. Doll and Hossner (1964) suggested that the suppressing effect of high K on Mg uptake may be due partially to reactions between applied K and soil components. Specifically, Mg^{2+} may be trapped in an inaccessible position within interlayers of collapsed plates of 2:1 lattice clays.

d. Percent Magnesium Saturation. The exchangeable-soil Mg level recommended for agronomic crop production by different soil-testing services ranges from 25 to 180 mg kg⁻¹, or approximately 10% saturation of the soil CEC. Fox and Piekielek (1984) reported that at least 10% saturation was required to obtain 2 g of Mg kg⁻¹ in corn silage grown on Ultisols and Alfisols studied. They indicated that 5% saturation of the soil CEC was adequate to produce 1 g of Mg kg⁻¹ in the ear leaf and grain yield was not decreased at this level. Stout and Bennet (1983) observed a slight corn grain yield increase to Mg application on an Inceptisol that had an exchangeable Mg level of 3.75% saturation of the CEC. At 5.65% Mg saturation there was no response. Soils that had <4% of the CEC saturated with Mg were Mg deficient for maximum yields of sudangrass and ladino clover (*Trifolium repens* L.) (Adams & Henderson, 1962). Three percent Mg saturation of a high CEC soil was not sufficient for maximum yields of alfalfa (McLean & Carbonell, 1972). They indicated that it was important to have a high level of Mg saturation of the CEC with adequate but not excessive levels of exchangeable K. Martin and Page (1969) reported that at 30, 50, and 100% base saturation, about 3 to 6% exchangeable Mg was associated with Mg-deficiency symptoms and reduced growth of sweet orange [*Citrus sinensis* (L.) Osb.] seedlings. About 7 to 13% exchangeable Mg was associated with mild Mg deficiency symptoms, but plant growth was not reduced. About 4% exchangeable Mg was critical for the Hanford soil (coarse-loamy, mixed, nonacid, thermic Typic Xerorthent). At this level, growth was not reduced but leaf Mg-deficiency symptoms appeared. Three to 4% exchangeable Mg in the Merriam soil (reclassified to Placentia series, a Typic Natrixeralf; L.J. Lund, 1989, personal communication) was sufficiently low to cause severe Mg-deficiency symptoms and reduced plant growth (Martin & Page, 1969).

e. Cation Ratio. Ratios of K/Mg reported as favorable for crop production range from 0.8:1 to 20:1. Ologunde and Sorensen (1982) indicated that as long as the absolute amounts of K and Mg in a sand culture growth medium were adequate to meet the demands of the plant, the K/Mg ratio could vary widely (1–25) without causing any adverse effect on plant dry matter production. The K/Mg ratio was not useful in predicting the amount of growth of sorghum (*Sorghum bicolor* L. Moench) in their study. Mulder (1950) noted in a review paper that deficiency symptoms appeared in apple (*Malus sylvestris* Mill) trees when the K/Mg ratio in the Morgan extract of the top 20 cm of soil was 2:1 to 1.6:1, while under normal trees it was 0.8:1.

Pratt et al. (1957) found no correlation between available Mg and soil K/Mg ratio in the 0 to 15 or 15 to 30 cm soil depths and suggested the K/Mg ratio of the 30 to 91 cm depth provided the best estimate of Mg availability to citrus. Similar results were reported by McCollock et al. (1957) who found a correlation of $r = 0.91$ between citrus leaf Mg and the exchangeable K/Mg ratio of the 46 to 76 cm soil depth. Their data indicated that additional Mg was needed to prevent Mg deficiency when the ratio of soil K/Mg exceeded 0.5. Charlesworth (1967) found the K/Mg ratio was better related to the Mg content of carrot leaves than exchangeable Mg in the 0 to 46 cm of soil depth. Batey (1967) concluded that the effectiveness of the K/Mg ratio depended on the crop, its stage of growth, climate, and soil depth, drainage, and structure. Slow-growing crops may tolerate a wider ratio of K/Mg in the soil than quick-growing, intensive, horticultural crops. He suggested maintaining K/Mg ratios of 2:1 or less in the soil by balancing soil K and K applications with dressings of kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) or other Mg-containing fertilizers to avoid Mg deficiency. Soils with low Mg availability ($< 100 \text{ mg kg}^{-1}$) and a pH of < 5.4 , or a K/Mg ratio > 4 were likely to be Mg deficient.

The Mg/K ratio has been evaluated in several studies (Adams & Henderson, 1962; McLean et al., 1983; Olson et al., 1982). The ratio of exchangeable Mg/K was not a better indicator of available Mg than percent Mg saturation of the soil CEC (Adams & Henderson, 1962). Olson et al. (1982) indicated that the Mg/K ratio varied from 2.2:1 to 6:1 with no significant effect on corn yield or change in available soil K after 7 yr on four major central U.S. Great Plains soils. McLean et al. (1983) evaluated corn, soybean, wheat, and alfalfa relative to Mg/K ratios and found no significant relationship between Mg/K ratio of the soil and yield of any of these crops.

The Mg concentration in ryegrass (*Lolium perenne* L.) was proportional to

$$(\sqrt{{}^a\text{Mg}})/[(\sqrt{{}^a\text{Ca} + \text{Mg}}) + (B{}^a\text{K})]$$

where ${}^a\text{Mg}$, ${}^a\text{Ca} + \text{Mg}$ and ${}^a\text{K}$ were the initial ion activities calculated from the composition of the equilibrium soil solution, and B is a proportionality factor determined by cations in the plant and cation activities in soil solution (Salmon, 1964). The Mg concentration in the grass was correlated ($r = 0.95$) with this ratio and explained some variations in Mg availability on different acid soils.

Hooper (1967) indicated that the Mg/Ca ratio was little better than exchangeable Mg for improving the correlation with Mg uptake. The correlation of Mg/Ca with herbage Mg was better in soils with pH > 6.5 .

Fox and Piekielek (1984) evaluated the Ca/Mg ratio and reported no reduction in corn yield at ratios from 1.8 to 36.9. Simson et al. (1979) reported that the Ca/Mg ratio could probably go below 0.5 before Mg toxicity or Ca deficiency would affect corn growth. Eckert and McLean (1981) indicated that the balance of cations in the soil was unimportant, except at the extremely wide ratios. At wide ratios, deficiencies of one element were caused by excesses of others, therefore, no best ratio existed for German millet or alfalfa. Olson

et al. (1982) concluded that cation balance was not an essential consideration in estimating crop nutrient needs for the yields obtained and soil conditions of their study.

II. SOIL TEST APPROACHES AND METHODS

A. Potassium

1. Rapid Chemical Extractions

Soil-testing laboratories generally rely on rapid methods of extraction and analysis to achieve the short turn-around time expected by clients. An estimate of exchangeable K, which usually includes soil solution K^+ , is the standard index of K availability in the USA and Canada. Exchangeable K is related to tissue K concentration (Fig. 8-6) and crop yields (Fig. 8-7) under many conditions. Even when the contribution of nonexchangeable K to plant nutrition is significant, exchangeable K has been closely correlated with uptake of K by plants (Doll & Lucas, 1973). Exchangeable K is determined by a variety of extractants (Fig. 8-8 and Table 8-4), most of which employ NH_4^+ or Na^+ as the cation to replace K^+ on exchange sites. Outlines of procedures used in the north-central and southern regions of the USA have been published (Dahnke, 1988; Johnson et al., 1984).

Determination of total exchangeable K requires exhaustive leaching or washing with 1.0 M ammonium acetate, pH 7.0 (Knudsen et al., 1982). This extractant has been used for more than 50 yr (Chapman & Kelley, 1930).

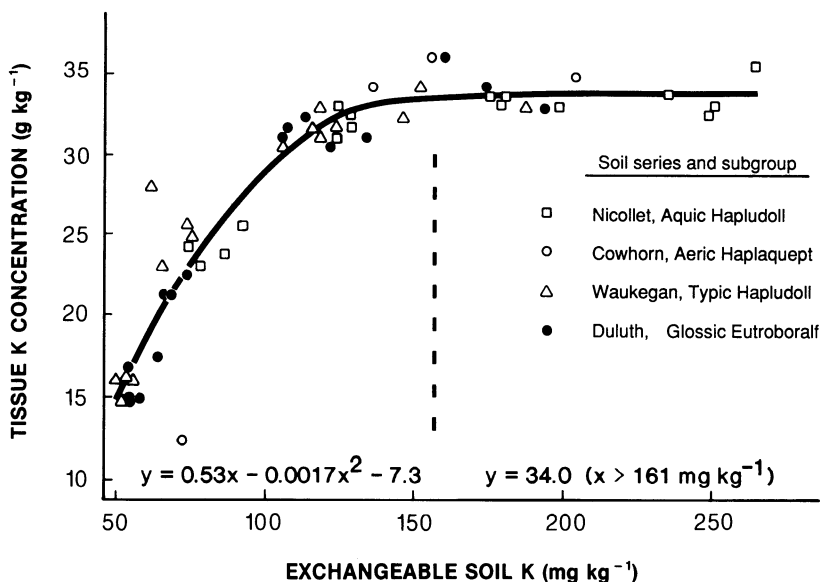


Fig. 8-6. Relationship between exchangeable soil K and tissue K concentration in birdsfoot trefoil (*Lotus corniculatus* L.) seedlings grown in pots for 42 d in the greenhouse (Russelle et al., 1989).

Typical soil-test procedures are designed to minimize extraction time and labor, while attaining adequate precision in results. Extraction at a 1:10 soil/solution ratio with vigorous shaking (at least 200 oscillations per minute) for 5 min is currently recommended for laboratories determining extractable soil K with neutral 1.0 M ammonium acetate in north-central USA (Knudsen et al., 1982). Shaking time has a variable impact on soil test results (Fig. 8-9).

Although neutral 1.0 M ammonium acetate has long been and is presently the most widely used extractant for K in public soil-testing laboratories, other extractants are gaining in popularity. Many of these solutions facilitate the removal of several elements in one extraction, and are referred to as “universal” extractants. Their use is complemented by the availability of multi-element analytical techniques such as ICP spectrometry.

Because of the chemistry regulating phytoavailability of other nutrient elements, such as P, Zn, and Mn, extracting solution composition and pH have been adjusted for the soils being analyzed; acidic solutions are typically used in neutral to acidic soils and alkaline solutions are usually used in neutral to calcareous soils (Fig. 8-8). Removal of exchangeable soil K is also affected by changes in solution composition, so new methods must be calibrated to crop response and not simply correlated with nutrient extraction by the old method.

Mehlich (1953) proposed the use of the double-acid (Mehlich I) extractant for P, K, Ca, Mg, Na, Mn, and Zn. It is used primarily in states on the Atlantic and Gulf Coasts, where soils are predominantly Ultisols, Inceptisols, and Spodosols (Fig. 8-8). Amounts of K, Ca, and Mg removed by the double acid extractant are closely correlated with, but usually lower than, amounts removed in neutral 1.0 M ammonium acetate. The double acid extractant removes excessive amounts of P in calcareous soils and in soils where apatite is the predominant source of P.

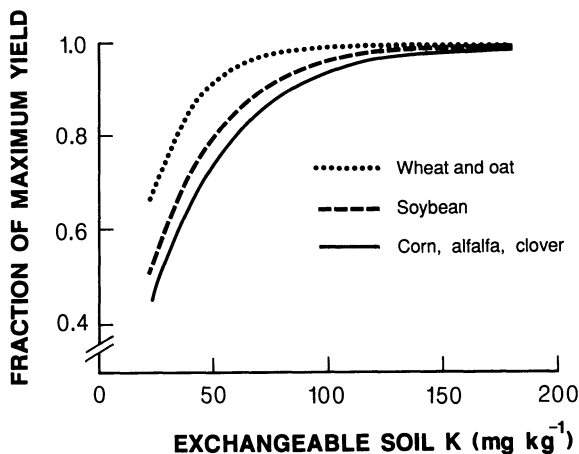


Fig. 8-7. Relationship between exchangeable K in topsoil and yield of several crops on soils with CEC < 12 cmol_c kg⁻¹. (Redrawn from Bray, 1945.)

Mehlich (1978) suggested a new extractant (Mehlich II), which provided improved results for P over a wider range of soils. Extraction of K, Ca, and Mg was also more closely related to the standard ammonium acetate extraction. However, the high concentration of Cl^- (0.21 M) was corrosive to laboratory equipment. No public soil-testing laboratories currently recommend the use of the Mehlich-II extractant.

Because of problems with corrosion and the desire to improve the reliability of Cu extraction, Mehlich (1984) designed an improved extractant by substituting nitrates for chlorides and by adding EDTA. Five states have adopted this extractant, and it is under investigation by several public and

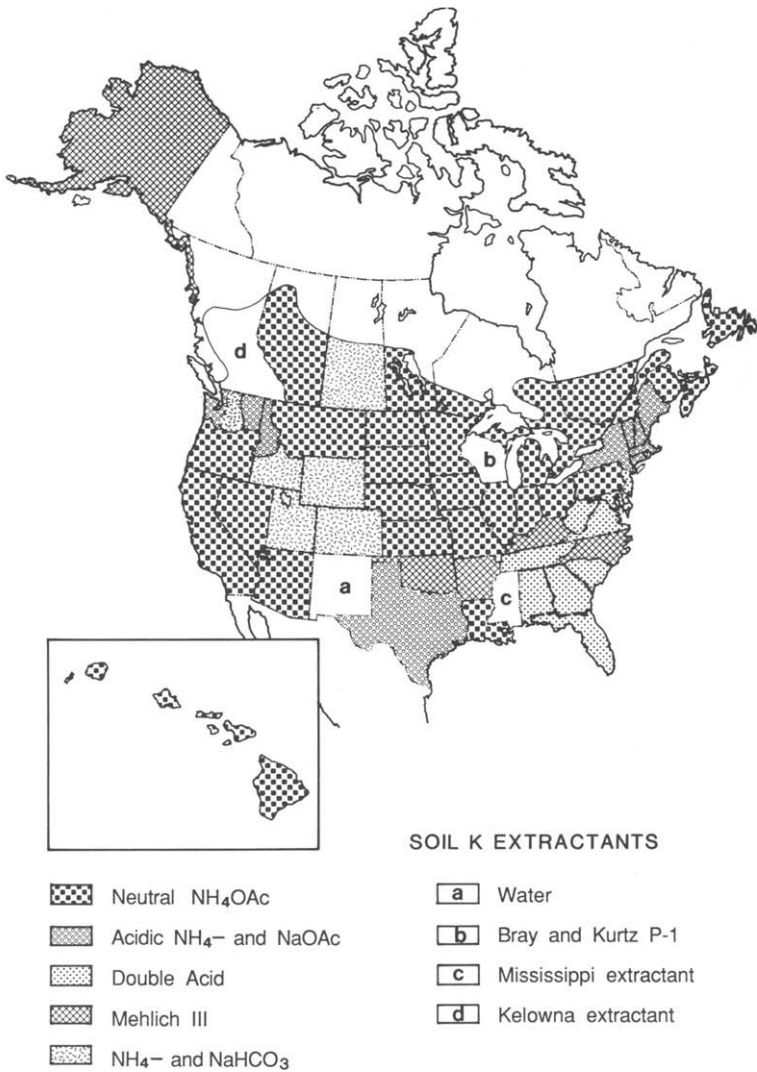


Fig. 8-8. Soil K extractants used or recommended by public soil-testing laboratories in the USA and Canada (from a survey conducted by Russelle).

Table 8-4. A selection of K-extraction methods used in the USA and Canada, 1988.

Method	Components	Concentration, mol L ⁻¹	pH	Soil/solution ratio	Extraction time	Reference
Ammonium acetate	CH ₃ COONH ₄	1.0	7.0	1:10	5 min	Knudsen et al., 1982
Baker	I. CH ₃ COONH ₄ II. KCl	1.0 2.5 × 10 ⁻⁴	7.0 7.3	1:10 1:10	30 min 24 h	-- Baker & Amacher, 1981
	MgCl ₂	10.0 × 10 ⁻⁴				
	CaCl ₂	50.0 × 10 ⁻⁴				
	DTPA†	4.0 × 10 ⁻⁴				
	TEA					
Bray and Kurtz P ₁	HCl	0.025	2.6	1:10	5 min	Knudsen & Beegle, 1988
	NH ₄ F	0.03				
Double acid (Mehlich I)	HCl	0.05	--	1:5	5 min	Mehlich, 1953
Kelowna	H ₂ SO ₄	0.0125				
	CH ₃ COOH	0.25	3.2	1:10	5 min	van Lierop, 1985
	NH ₄ F	0.015				
Mehlich III	HNO ₃	0.013				
	NH ₄ F	0.015	2.5	1:10	5 min	Mehlich, 1984
	CH ₃ COOH	0.2				
	NH ₄ NO ₃	0.25				
	EDTA	0.001				
Mississippi	I. HCl	0.05	--	1:1	10 min	Lancaster, 1980
	II. NH ₄ F	0.037	4.0	1:4	10 min	
	CH ₃ COOH	1.57				
	CH ₂ (COOH) ₂	0.0625				
	CH ₂ CHOH(COOH) ₂	0.0933				
	AlCl ₃	0.0124				
Morgan	CH ₃ COOH	0.52	4.8	1:5	30 min	Lunt et al., 1950
	CH ₃ COONa	0.73				
Modified Morgan (one example)	CH ₃ COOH	1.25	4.8	1:5	15 min	McIntosh, 1969
Olsen	NH ₄ OH	0.62				
	NaHCO ₃	0.5	8.5	1:20	30 min	Olsen et al., 1954
Soltanpour	NH ₄ HCO ₃	1.0	7.6	1:2	15 min	Soltanpour & Schwab, 1977
	DTPA	0.005				
Texas	CH ₃ COONH ₄	1.4	4.2	1:20	60 min	A.B. Onken 1980, unpublished data (listed in Johnson et al., 1984)
	HCl	1.0				
	EDTA	0.025				

† DTPA = diethylenetriaminepentaacetic acid, TEA = triethanolamine, and EDTA = ethylenediaminetetraacetic acid.

private soil-testing laboratories. It is apparently useful over a broad range of soils and climatic conditions (Fig. 8-8) and has obvious advantages as a universal extractant (Hanlon & Johnson, 1984). Potassium removal is about 20% greater than, but highly correlated with the standard ammonium acetate method (J.S. Harrison and V.W. Case, 1988, personal communication). However, salt deposition in nebulizers of certain brands of atomic absorption and ICP spectrometers has occurred with the Mehlich-III extractant.

Onken et al. (1980) reported that P extracted by EDTA solution was significantly related ($R^2 = 0.71$) to grain sorghum yield response in the field. Since that time, 0.025 M HEDTA has been added to the 1.4 M $\text{CH}_3\text{COONH}_4$ -1.0 M HCl (pH 4.2) extracting solution in Texas. This solution is used as a universal extractant for K, Ca, Mg, and other plant nutrients (Hons et al., 1990; Johnson et al., 1984). The initial problem with salt deposition has been eliminated by modification of the instrument nebulizer (H.D. Pennington, 1988, personal communication).

Soltanpour and Schwab (1977) and Soltanpour and Workman (1979) proposed the use of 1.0 M NH_4HCO_3 with 0.005 M DTPA, pH 7.6, as an

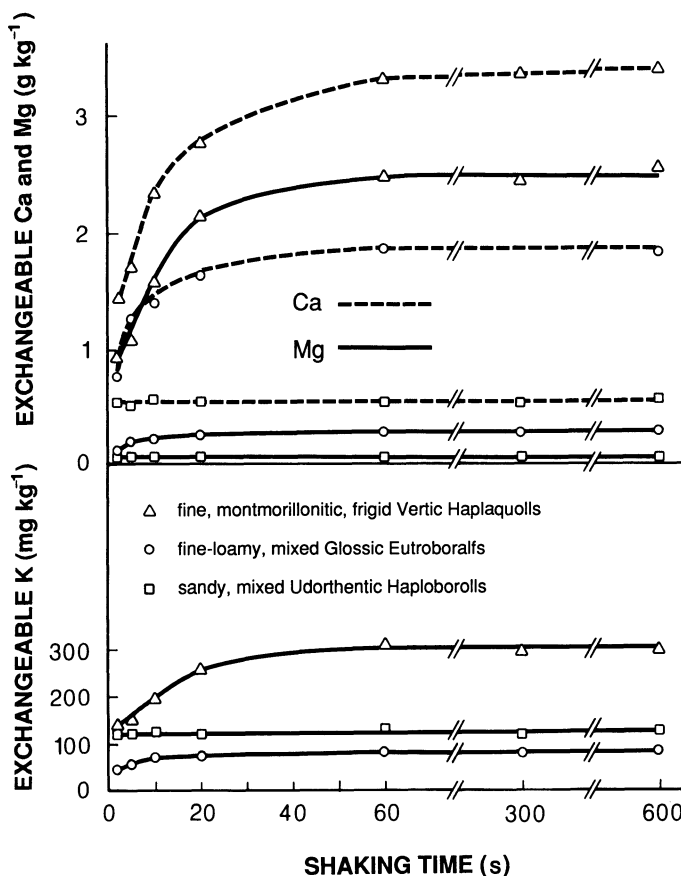


Fig. 8-9. Relationship between shaking time in neutral 1 M ammonium acetate and K, Ca, and Mg soil test results (M.P. Russelle and I.T. Aighewi, 1985, unpublished data).

extractant for $\text{NO}_3\text{-N}$, P, K, Zn, Fe, Cu, and Mn from alkaline soils. They tested a group of 481 soil samples, having diverse chemical properties. Soil test results with the new extractant were well correlated with standard extraction techniques, although the limits between low, medium, and high soil test levels had to be adjusted for several elements. No change was required for the soil K test. This extractant is presently used in Colorado and Wyoming (Fig. 8-8). Sodium bicarbonate (Olsen et al., 1954) is used to extract alkaline soils in three western states and in Saskatchewan. However, analysis of Ca and Mg in this extractant by atomic absorption spectroscopy is difficult due to the milky precipitate that forms when lanthanum or strontium chloride is added for ionization suppression to increase Ca and Mg sensitivity.

The Morgan extractant (Table 8-4) was designed to simulate the dissolution of soil constituents by dissolved CO_2 (Lunt et al., 1950). It has been used extensively in the northeastern states and to some extent in the Pacific Northwest as a universal extractant for P, K, Ca, Mg, and N. Four states now use the Morgan extractant (Fig. 8-8). Variations of the Morgan solution use NH_4^+ in place of Na^+ to effect more complete displacement of K from clays (McIntosh, 1969). These variations are generally referred to as "modified Morgan" extractants and are used in a few northeastern states. Other extractants currently used include water (New Mexico), Bray and Kurtz P_1 (Wisconsin) (Bray & Kurtz, 1945), the Kelowna extractant (British Columbia), and the Mississippi extractant (Table 8-4).

Dilute or concentrated acids will remove both exchangeable K and a fraction of nonexchangeable K. Hunter and Pratt (1957) demonstrated that soil K extraction with H_2SO_4 could reliably predict K removal by various crops in field and greenhouse conditions. Extracting K by refluxing with HCl was the most precise and fastest means of determining soil K status, including the rate and amount of fixed K release (Singh et al., 1983). However, McCallister (1985) has shown that K extraction with boiling HNO_3 (Wood & DeTurk, 1940; Brown et al., 1973) or sodium tetraphenylboron (Scott et al., 1960; Schulte & Corey, 1965) do not mimic natural feldspar weathering, even though they may provide estimates of plant-available soil K. Hazards associated with use of concentrated acids in routine soil testing have limited the adoption of these methods.

Use of cation exchange resins to remove plant-available soil K has been suggested (e.g., Haagsma & Miller, 1963), but has met with variable success (Skogley & Haby, 1981; Schaff & Skogley, 1982a; Singh et al., 1983). McLean and Watson (1985) have presented an excellent discussion of these and other approaches to soil K extraction. Skogley and Georgitis (1988) reported results of continued research on development of a resin approach as a universal extractant.

2. Incubation and Displacement Techniques

A substantial number of experiments have confirmed that exchangeable K in the topsoil can be used to predict fertilizer K response under many conditions (e.g., Havlin & Westfall, 1985). Under other conditions, however,

exchangeable K has been a poor indicator of crop response. For example, Skogley and Haby (1981) found no soil test method for K to be adequate for the cool, dry, high-exchangeable K soils of Montana. Application of KCl significantly decreased the incidence of dryland common root rot (*Fusarium* spp.) in dryland barley (*Hordeum vulgare* L.) in Montana (Garvin et al., 1981). That K_2SO_4 in the same experiment had no effect on this root rot, suggested that disease reduction because of Cl^- could be partially responsible for the observed yield increases attributed to K in these high-exchangeable K Northern Great Plains soils. Evidence from South Dakota confirmed that yield response to KCl fertilizer on high K-testing soils is due, in part, to improved Cl nutrition (Fixen et al., 1986). On low-exchangeable K, sandy east Texas Timberlands soils and Coastal Plains soils of the southeastern USA, lack of initial crop response to applied K was because of rapid release of nonexchangeable K from micaceous minerals in the subsoil (Hons et al., 1976; Yuan et al., 1976). Due to their low clay content, intensive cropping of the deeper sands for several years soon depletes plant-available subsoil K. Barbarick (1985) suggested that alfalfa response to K_2SO_4 on Colorado soils with high-exchangeable K throughout the profile may be because of depression of Na absorption. Only 13% of the variability in K uptake by corn was accounted for by exchangeable K at 51 field sites in Wisconsin (Wietholter, 1983). Considering the complexity of and the interactions among the factors affecting K availability to plants, it is remarkable that simple measures of soil K bear any relationship to K uptake and yield.

Several methods have been proposed to permit more thorough characterization of soil K availability. These methods are not generally used in routine soil testing in the USA and Canada, but may be used in the future to more precisely estimate K-fertilizer requirements for groups of soils and specific crops.

The soil solution is the major pool of K^+ available to plants. Potassium in solution tends to be in equilibrium with K on exchange sites; if addition to (e.g., via fertilization) or removal from (e.g., via absorption by roots) solution occurs, some K^+ will attach to or be released from the exchange sites. Dissolution or formation of hydrous micas will also occur in response to changes in soil solution K^+ concentrations (McLean, 1978; Dubetz & Dudas, 1981; Sparks & Huang, 1985).

Changes in exchangeable K must be balanced by opposite changes in other exchangeable cations, notably Ca and Mg. Because changes in K availability in the soil do not occur independently of other cations, it is appropriate to express the status of K relative to the status of the dominant cations (Schofield, 1947). The activity, or effective concentration, of K^+ in soil solution divided by the combined activity of Ca^{2+} and Mg^{2+} is called the activity ratio (AR). This ratio facilitates comparison of different soils, because the K activity is expressed at comparable $Ca^{2+} + Mg^{2+}$ activity.

Several parameters related to K availability can be derived from the relationship between the AR of K^+ (intensity) and the amount of exchangeable K (quantity) when a soil is equilibrated with different amounts of added K^+ (e.g., Beckett, 1964b; Sparks & Huang, 1985). This relationship is called the

quantity/intensity (Q/I) curve. The three most important parameters of this relationship are: (i) the X intercept, which indicates the equilibrium AR for K^+ (AR_e); (ii) the Y intercept, which is an estimate of labile or exchangeable K using this procedure; and, (iii) the slope of the curve at AR_e , which is called the potential buffering capacity (PBC). The greater the PBC, the less change will occur with K addition or removal.

The Q/I approach has been useful in explaining K supply in particular soils (Sparks & Liebhards, 1981) or in related soils (Zandstra & MacKenzie, 1968), but is not applicable to soils of widely different Ca and Mg contents (Beckett, 1964a; Quemener, 1979). Parra and Torrent (1983) suggested a method of more rapidly determining Q/I relationships. A greatly simplified Q/I analysis provided good estimates of K uptake by white clover (During & Duganzich, 1979).

Goedert and Corey (1973) used a single equilibration with 0.001 M $SrCl_2$ to estimate ion activity, exchangeable level, buffering capacity, and AR of K^+ , Ca^{2+} , and Mg^{2+} . Wietholter (1983) improved on their approach by using 0.004 M $Sr(NO_3)_2$. He used a diffusion-controlled K uptake model to predict K accumulation in field-grown corn and was able to account for 58% of the variability in measured K uptake. Further research on this extractant is underway at the Univ. of Wisconsin.

Several comprehensive models of plant nutrient availability have been developed (e.g., Barber, 1984). Use of such models will likely become more common in areas where important climatic factors are not too variable and where soil factors, especially K buffer power and the effective diffusion coefficient for K^+ , can be reasonably estimated from existing databases such as soil survey information. Critical plant parameters, such as root growth rate, nutrient uptake activity, and effective radius, must be determined for different crop species and genotypes. This model was less successful in predicting K uptake by alfalfa seedlings (Aighewi, 1988) than has been reported for corn (Shaw et al., 1983) or soybean (Silverbush & Barber, 1983). Mechanistic models will be able to provide useful predictions only to the extent that we understand the system being modeled and that we provide accurate and precise values for the input variables.

Baker's method of soil testing incorporates estimates of quantity and intensity (Baker & Amacher, 1981). Quantity is determined by extraction with standard solutions (e.g., neutral 1 M ammonium acetate for K, Ca, and Mg) or by equilibration with the Baker soil test solution, and thermodynamic analysis is used to calculate availability (intensity). The Baker soil test solution (Table 8-4) was designed to represent optimum concentrations of K^+ , Ca^{2+} , and Mg^{2+} in an ideal soil. Reduction of the K^+ concentration in solution after a 24-h incubation indicates that insufficient K is available to maintain the optimum concentration. The Baker method is presently being used only in Maine and in a small lab in Pennsylvania, due to the seeming complexity of calculations and the need, as with all soil-testing procedures, of correlation and calibration data for different soil conditions. The complexity of the calculations should not be a hindrance because they can be made rapidly by computer.

McLean's method uses the classical (Fig. 8-7) or updated response curves for field crops with standard ammonium acetate extraction of exchangeable K, but adjusts the fertilizer K recommendation by fixation factors specific to various groups of soils (McLean et al., 1982; McLean & Watson, 1985). The fixation factor can be determined by equilibrating duplicate soil samples for 2 h with and without a known amount of added K, followed by measurement of exchangeable K. The non-amended sample provides a measure of the existing K level; the decrease in K recovered in the amended sample is an index of the K-fixation capacity. These 2-h values can more accurately reflect field conditions by adjusting them to the fixation measured after 8 wk of incubation (Moorhead & McLean, 1985). The relationships between short- and long-term incubations need be determined only once and can be limited to selected soil groups representative of the region from which samples are received.

McLean's method has the potential of more precisely predicting K fertilizer requirements for individual soils because it does not rely on the standard, but inaccurate, 60% recovery figure used in many recommendations. Soils vary from <20% to >90% fertilizer K recovery. The primary disadvantage is that two extractions per soil sample are needed, requiring significantly more bench space, equipment, reagents, and labor.

3. Electro-ultrafiltration

The technique of electro-ultrafiltration (EUF) was developed more than 60 yr ago by Bechold (cited by Nemeth, 1979). It combined the methods of electrodialysis and ultrafiltration, both of which had been used to separate dissolved nutrients from soil. Most of the current literature on this method is by K. Nemeth and colleagues (e.g., Nemeth, 1979, 1982; Nemeth et al., 1970). In 1981, EUF was being used in more than 20 countries either in research or in soil-testing laboratories (Nemeth, 1982). Since 1974, the Tulln Sugar Factory in Austria has used EUF as a routine method of extracting nutrient elements important to sugarbeet producers. They extract up to 20 000 soil samples per year. The Southern German Sugar Company (Rain, West Germany) has 26 EUF units and has computerized the collection and interpretation of data from ICP spectrometers and various N analyses (J.T. Moraghan, 1988, personal communication).

Like universal extractants, EUF provides a method of extracting several elements simultaneously, including NH_4^+ -N, NO_3^- -N, P, K, Ca, Mg, Na, S, B, Mn, and Zn. The apparatus consists of three cylindrical compartments or "cells" connected end to end and separated by microfiber filters and platinum electrodes. A 1:10 soil/solution suspension is stirred in the central cell while voltage is applied to the electrodes. Vacuum in the outer cells withdraws water and dissolved constituents from the central cell; water is added continuously to the suspension to maintain a 1:10 ratio. Voltage and suspension temperature are increased during extraction to remove the less labile forms of the elements. Fractions are often collected from the outer cells at 5-min intervals over 35 min, but for routine soil-testing applications, vari-

ous groups of fractions are combined before analysis, e.g., 0 to 10 min, 10 to 30 min, and 30 to 35 min. Fractions collected on the anode and cathode sides are usually combined before analysis, because mass flow causes incomplete separation of charged species during the initial phases of extraction. The fractions are analyzed by standard techniques for the elements of interest.

An example of a typical K^+ extraction curve is shown in Fig. 8-10. The amount of K^+ recovered after 5 min at 50 V and 20°C is approximately equal to the K^+ in soil solution (Nemeth, 1979; van Lierop & Tran, 1985). The K^+ recovered in the first 10 min (5 min at 50 V and 5 min at 200 V) is closely correlated with the AR_e , but should not be regarded as a measurement of intensity, because it apparently includes some exchangeable K (Sinclair, 1980). Amounts of K^+ extracted by EUF over a longer period (5 min at 50 V and 25 min at 200 V) were closely correlated with K extracted by ammonium acetate, double acid, and Mehlich-II techniques, but were not as closely related to K^+ removed by $SrCl_2$ (Table 8-5). Potassium extracted during the last 5 min at 400 V and 80°C reflects the buffering capacity of the soil, with little release from kaolinitic and substantial release from smectitic clays (Nemeth, 1979).

Fertilizer requirements vary with clay content (Fig. 8-11) and the relationship between easily and slowly available K. The values in Fig. 8-11 were developed on central European soils and may not be applicable for soils of different parent materials and development. Certainly, the rates required for clay soils that have low amounts of EUF extractable K^+ would be prohibitively expensive for contemporary North American farms.

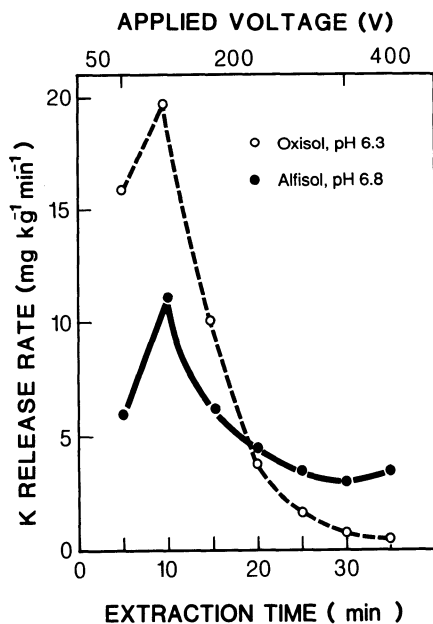


Fig. 8-10. Typical EUF-K release rate curves for two soils of similar exchangeable K content (Oxisol, 262 mg kg⁻¹; Alfisol, 238 mg kg⁻¹), but different K release patterns. (Redrawn from Nemeth, 1979.)

Table 8-5. Relationship between soil K determined after chemical extraction and after EUF extraction (5 min at 50 V and 25 min at 200 V) for 102 soils (van Lierop & Tran, 1985).

Extractant (X)	Potassium concentration range mg kg ⁻¹	Estimate of EUF-K (Y)	r ²	SE†
Ammonium acetate 1.0 M, pH 7.0	8-250	Y = 0.78X - 13.1	0.85	16.9
Double acid	15-200	Y = 1.0X + 3.2	0.90	13.4
Mehlich II	8-240	Y = 0.80X - 8.6	0.88	16.8
Strontium chloride 0.01 M	1-95	Y = 1.51X + 13.7	0.76	21.2

†SE = Standard error of the estimate of Y.

This method of soil nutrient extraction has received little attention in the USA and Canada, although a few researchers have begun to evaluate EUF. Commercially available automated units cost more than \$20 000 (U.S. dollars) in 1988. One EUF unit can be used to extract only 8 to 16 samples per day, depending on extraction time. The expense of purchasing several

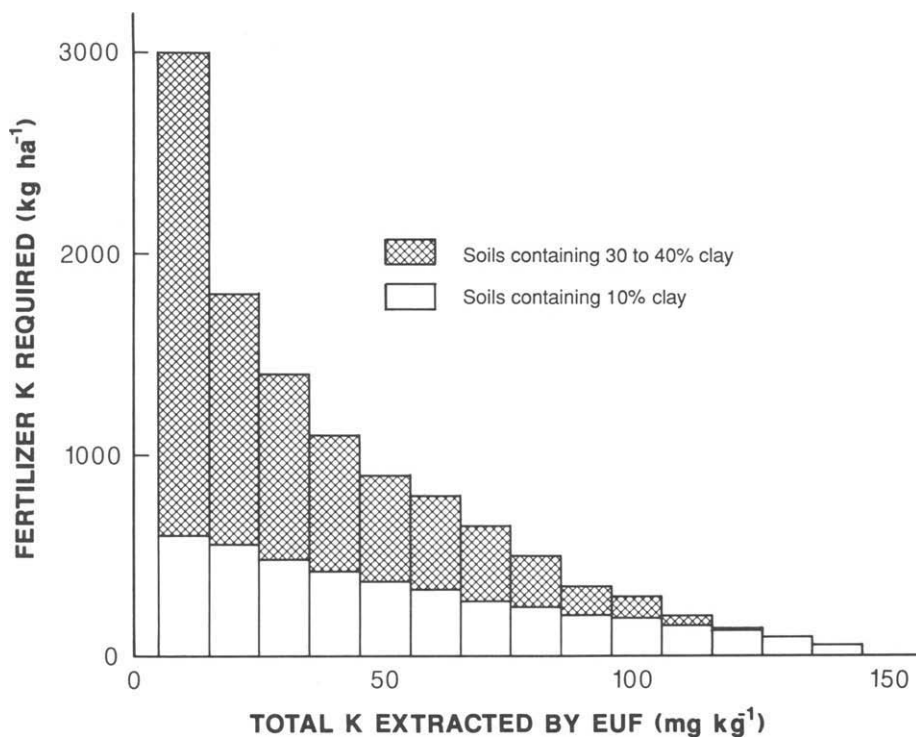


Fig. 8-11. Quantity of fertilizer K needed to increase soil EUF-K values to 150 mg kg⁻¹ as related to clay and measured EUF-K content. (Adapted from Nemeth, 1979.)

of these units, the necessity of employing a highly trained, technical expert to supervise the analyses of these chemically complex samples, and the need for extensive calibration data for North American conditions are definite impediments to the expansion of this method. van Lierop and Tran (1985) concluded that little additional information could be obtained by EUF compared to less-expensive and labor-intensive chemical procedures. Others disagree (see Nemeth, 1982). More research is needed to resolve these issues.

4. Sampling and Sample Handling

The effect of soil moisture content on exchangeable-K concentrations has been recognized since at least 1928 (Steenkamp, 1928). The direction of change in exchangeable K upon drying depends on the mineralogy, equilibrium concentration of K^+ , and the deviation from the equilibrium concentration at sampling. Haby (1975) analyzed the 0- to 15- and 15- to 30-cm horizons of 18 Montana soils, and found that no change occurred during air drying when exchangeable K in field moist samples was 421 mg kg^{-1} (Fig. 8-12). Fixation occurred during drying at higher K levels, release at lower K levels. If a similar value is characteristic of soils from more humid regions, most would be expected to release K upon drying, because few fields would have soil test levels approaching 1000 kg ha^{-1} .

Dramatic changes in exchangeable K can occur in samples as the moisture content of the air-dry conditions changes with relative humidity (Fig. 8-13; Luebs et al., 1956). The slopes of the curves in Fig. 8-13 range from -360 to $-960 \text{ mg of K kg}^{-1} \text{ water}$ at the air-dry moisture content. Small changes

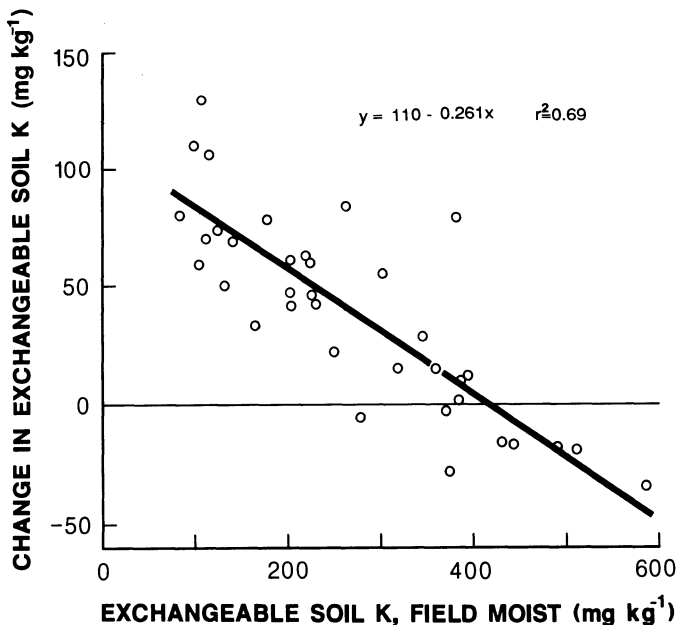


Fig. 8-12. Effect of initial exchangeable K content of field-moist soils of the northern Great Plains on K release or fixation upon air drying at 25°C. (Adapted from Haby, 1975.)

in relative humidity during drying can alter soil test results, with greater effects occurring in finer-textured soils. The effect of air drying is more pronounced in K-fertilized soil than in nonfertilized soil (Fig. 8-14). Differences between control and fertilized soils are often greater for field-moist samples than for dried samples (Grava et al., 1961). Extractable K was linearly related to soil moisture content in 9 of 10 Montana soils evaluated (Haby et al., 1988).

Although air-drying soils is known to cause unpredictable changes in exchangeable K, field-moist soil samples are not being routinely analyzed by any public laboratory at present. For more than 20 yr, the public laboratory in Iowa used field-moist samples for K analysis, but has begun drying all samples. Sample storage is simplified and subsamples are less variable. Changes in exchangeable K because of drying are smaller in topsoils than in subsoils, because topsoils usually contain less clay. Analytical results of both dry and moist samples generally reflect previous management of topsoils. Drying and wetting, and, in northern climates, freezing and thawing cycles, are also common in topsoils. Therefore, air drying of topsoil samples may not be an unreasonable treatment. Oven-drying soil samples, even

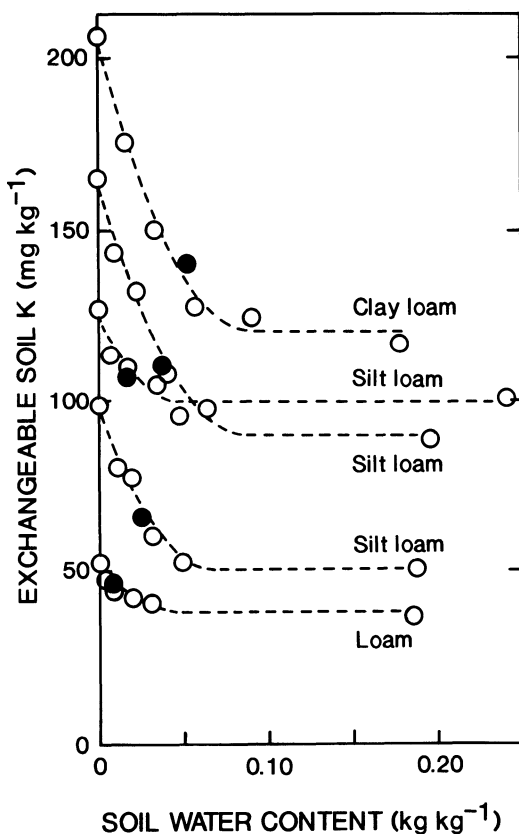


Fig. 8-13. Relationship between exchangeable-K concentration and soil moisture content of several Illinois topsoils (R.A. Bohannon and T.R. Peck, 1957, unpublished data). Closed circles indicate air-dry condition for each soil (25°C at about 50% relative humidity).

as low as 60°C, for K analysis should be avoided because this more severe drying causes greater K release (Haby et al., 1988).

Variations in soil test values for K over time should be expected in soils containing micas, vermiculite, or smectites (e.g., Grava et al., 1961; Fig. 8-14). These changes occur because of altered moisture content, freezing and thawing (which are essentially changes in soil moisture content), equilibration of exchangeable and nonexchangeable pools of K after K^+ addition or removal, equilibrium reactions after changes in the concentration of other cations, uptake and release of K^+ from plants and animals (including bio-cycling of subsoil K to the topsoil [c.f., James et al., 1975]), and leaching. Exchangeable K contents will reflect the net effect of these contrasting mechanisms. Changes in soil solution K^+ will be more extreme than alteration of exchangeable K during periods of plant growth, whereas changes in less labile forms of K could be expected to be rather small over the course of 1 or 2 yr.

Rapid increases in exchangeable K occur after fertilization, but concentrations typically decline during the growing season (Fig. 8-14). Similar decreases in nonfertilized soil also occur, but are less pronounced. In most

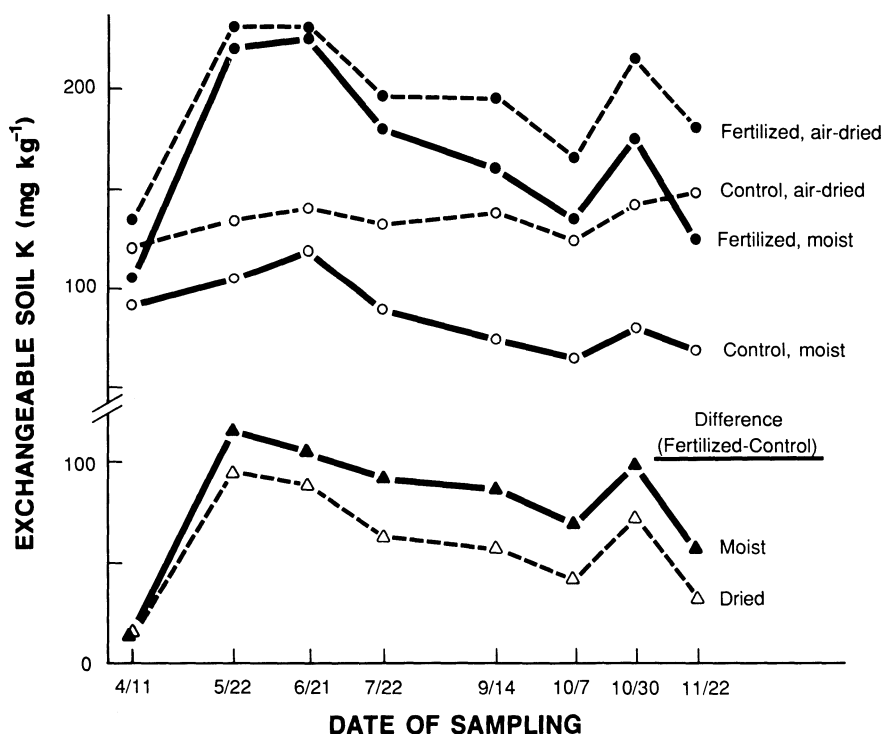


Fig. 8-14. Effect of sampling date and air drying on exchangeable K in the Ap horizon of an Aquic Hapludoll. Fertilized plots had received spring broadcast K applications of $74 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for 3 yr, including the year of sampling, and corn was grown on the plots each year. (Adapted from Grava et al., 1961.)

Canadian provinces and the northern USA, maximum exchangeable-K concentration in unamended soils will generally occur during winter due to freezing. This conclusion has been demonstrated in Illinois (T.R. Peck, 1988, personal communication) and Ohio (Lockman & Molloy, 1984). Because changes in exchangeable K may be appreciable and because we are not yet able to predict these changes (Sparks & Huang, 1985), soil samples should be taken at the same time of year to reduce time-dependent variability.

B. Calcium and Magnesium

The most common extractant for determining what is considered exchangeable Ca and Mg from soils is molar ammonium acetate at pH 7.0 (Lanyon & Heald, 1982). Most determinations of exchangeable soil Ca and Mg are made by high-temperature flame analysis using atomic absorption or ICP emission spectrometry. Ammonium and acetate are volatile in the flame, leaving no salt residue on the burners of these instruments.

Many reports discuss the relationship of a soil-extracted plant nutrient to plant uptake of the particular nutrient under consideration. Much of the crop response-soil test calibration research has been conducted under simulated conditions. Because of the many climatic and soil factors that affect plant availability of Ca and Mg, the amounts of these nutrients removed from a soil by a particular extractant must be correlated with field crop response to applied Ca or Mg in order for that soil extractant to accurately predict the crop's nutrient needs.

Calcium soil test levels and analytical methods used to predict availability of Ca to plants have not received the attention extended to Mg. Scientists and professional agricultural consultants generally agree that Ca availability to plants is not a problem in alkaline soils. Increasing acidity lowers exchangeable soil Ca. It has been well demonstrated that Al or Mn will often become toxic in acid soils before Ca concentrations become deficient. Maintenance of a favorable soil pH by limestone application to acid soils also provides adequate Ca for plant growth.

In contrast to Ca, research on soil test methods for Mg has been extensive for two reasons: (i) to predict crop yield response to applied Mg, and (ii) to predict Mg uptake by the plant to prevent hypomagnesaemia in ruminant animals. Chemical extractants evaluated for exchangeable Mg are many and include use of dilute salt solutions, acidified salt solutions, and dilute acids. MacDonald et al. (1978) correlated molar ammonium acetate-acetic acid, pH 4.8, with Morgan's solution (Table 8-4) to find a method that would be noncorrosive to the flame burner tip. The two methods extracted similar concentrations of Ca and Mg over a soil sample pH range of 4.4 to 7.8. Hooper (1967) found that Morgan's reagent at a soil/extractant ratio of 1:5 (wide ratio) extracted the most Mg. Molar ammonium nitrate at 1:5 soil/extractant and molar ammonium acetate at 1:25 extracted similar amounts of Mg. Morgan's reagent, narrow range (1:2, soil/extractant), shaken for 2 min extracted only two-thirds the Mg as did the wide range.

Calcium chloride removed only about one-half the Mg extracted by Morgan's reagent (wide ratio), ammonium nitrate, and ammonium acetate.

Other methods evaluated for available soil Mg include 0.05 *M* NaCl at a 1:5 ratio (Reith, 1967), neutral *M* ammonium acetate at a 1:5 ratio (Fox & Piekielek, 1984), and 1 *M* sodium acetate at pH 7 and pH 1 (Rice & Kamprath, 1968). Farina et al. (1980) found that 0.01 *M* CaCl₂ extracted lower amounts of Mg than did neutral *M* ammonium acetate. These scientists questioned the predictive value of exchangeable Mg as an index of plant availability because drastic decreases in exchangeable Mg were not accompanied by reduced Mg absorption.

III. CALIBRATION AND INTERPRETATION OF SOIL TESTS

There are basically two philosophies of soil test interpretation used by soil-testing organizations to arrive at fertilizer recommendations for K, Ca, and Mg: (i) the nutrient sufficiency level concept and (ii) the nutrient maintenance level concept.

A. Sufficiency Level

In the sufficiency level concept, there are definable levels of individual nutrients in the soil below which crops will respond to added fertilizers with some probability and above which they likely will not respond (Eckert, 1987). It has come from long-term calibration of soil tests with field yield response data establishing ranges of response assured, likely, possible, and unlikely, otherwise expressed as very low, low, medium, and high nutrient levels, respectively (Olsen et al., 1954; Olson et al., 1954). Some measure of the buffering capacities of individual soils is necessary to allow for reasonable soil buildup recommendations (Eckert, 1987), but the main objective of recommendations based on the sufficiency level concept is to "fertilize the plant." The sufficiency level concept of soil test interpretation requires the development of extensive databases from field trials that relate yield response of crops to fertilizer application on soils with different initial soil test nutrient levels. These databases are all too often poorly organized, no longer available for review, or several decades old. Field calibration research is expensive, time consuming, labor intensive, and not always conducive to publication—all of which strongly inhibit the development and maintenance of comprehensive databases. Although criticisms are made about the lack of relevance of calibration equations, they are frequently adequate to sustain high yields and to maximize profit (Olson et al., 1982).

B. Maintenance Level

The maintenance level concept is one of "fertilizing the soil." Adequate nutrient is applied annually to replace that which is expected to be used by the crop, plus some extra to increase the soil test level. Once the soil test

reaches the optimum high or very high levels, a maintenance application equal to the amount removed by the crop is applied to prevent the crop from lowering soil nutrient reserves. Soil test calibration for the maintenance level concept may include knowledge of the fixation capacity of a given soil for various nutrients, but is generally based on a standard value for the fixation capacity. Values for crop removal are usually calculated from average elemental concentrations and estimated or measured yields.

Optimum soil test levels can be based simply on extractable concentrations or on the ratio of extractable nutrients to one another. This "conservation" of a soil's nutrient-supplying capacity has strong appeal but discounts the economic aspect to the farmer in those situations where the soil's delivery capacity of a given nutrient may be adequate for top yields for some years to come (e.g., K in Houston Black clay in Texas).

The BCSR concept is used by some who advocate the maintenance approach. In a discussion of the BCSR concept, a distinction must be made between it and basic cation saturation of the soil CEC. With the BCSR concept, attempts are made to determine the amounts of fertilizer K, Ca, and Mg from ratios of these nutrients in the soil sample analyzed without knowledge of the soil CEC. Soil CEC must be known to compute the basic cation saturation percentage.

Numerous experiments during the past 40 yr have demonstrated that use of the BCSR approach alone in making fertilizer recommendations is both scientifically and economically questionable (Hunter, 1949; Key et al., 1955; Geraldson, 1957; Salmon, 1964; McLean & Carbonel, 1972; Claassen & Wilcox, 1974; Simson et al., 1979; Schulte et al., 1981; Eckert & McLean, 1981; Olson et al., 1982; Donohue, 1983; McLean et al., 1983; Fox & Piekielek, 1984). According to Leibhardt (1981), recommendations based on cation saturation percentages of 75% Ca, 15% Mg, and 2 to 5% K and the resulting cation ratios are not warranted, and may result in reduced yields, increased fertilizer costs, or both. Use of the BCSR typically increases fertilizer recommendations compared to other approaches. This method also ignores the selectivity that plants demonstrate during absorption of ions from soil solution.

McLean et al. (1982) have suggested that fertilizer recommendations could be based on a combination of Fisher's (1974) approach and short-term fertilizer recovery tests. This method assumes there is an optimum exchangeable K concentration in soil which varies positively with CEC. Fertilizer recommendations are calculated by (i) determining the difference in exchangeable K of the soil sample and the desired exchangeable K level, and (ii) dividing by the predicted recovery of added K. Potassium recovery varies with soil clay content and mineralogy (McLean, 1978; McLean et al., 1982; Stout, 1982). McLean's analytical method was discussed in section II.A.2.

IV. SOIL TEST LEVELS FOR ADEQUACY

A. Potassium

In the survey of public soil-testing laboratories, respondents were asked for general soil K test levels deemed adequate for maximum yield of different crops. As expected, these minimum adequate levels vary among the laboratories. States and provinces with the highest minimum values for corn (>200 mg of K kg^{-1}) are British Columbia, Manitoba, Missouri, Montana, Ohio, Quebec, and Wisconsin. Those with the lowest minimum values for adequate soil K (<110 mg of K kg^{-1}) include Alabama, Colorado, Delaware, Idaho, Massachusetts, Pennsylvania, South Carolina, and Utah.

Minimum adequate soil test levels vary with crop, soil, and management. In Minnesota, fertilizer K is not recommended for high yields of sugarbeets (*Beta vulgaris* L.), corn, and alfalfa on soils testing >100 , 150 , and 175 mg kg^{-1} , respectively (e.g., Fig. 8-15; Rehm et al., 1985). In Alabama, minimum adequate soil K test levels for corn must be above the medium level of 40 , 60 , or 80 mg kg^{-1} , for noncalcareous soils with CEC ranges of 0 to 4.6 , 4.6 to 9.0 , or >9.0 $\text{cmol}_c \text{ kg}^{-1}$, respectively (Cope et al., 1981). Addition of K fertilizer to alfalfa and corn is recommended in New York if soil K test levels are below the very high zone that begins at 150 mg kg^{-1} in fine-textured lacustrine sediments, and at 270 mg kg^{-1} in coarse-textured glacial

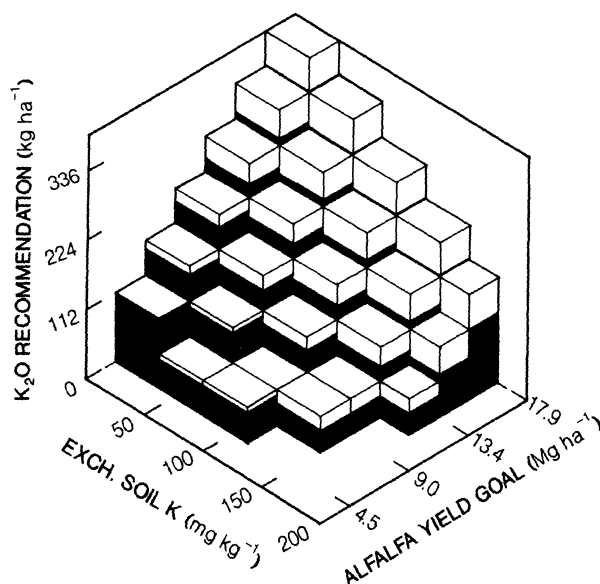


Fig. 8-15. Fertilizer K recommendations for alfalfa in Minnesota for different soil test K levels and yield goals. (Adapted from Rehm et al., 1985.) Dark columns are recommendations for fine- to medium-textured soils; light columns indicate additional fertilizer rates for coarse-textured soils.

till or outwash with low K reserves (Anonymous, 1984). Topdressed K fertilizer is recommended for alfalfa in Arkansas regardless of soil test levels (W.E. Sabbe, 1988, personal communication).

These few examples indicate the wide range of approaches to soil test interpretation and K-fertilizer recommendation provided by public soil-testing laboratories. Private soil-testing laboratories promote still other perspectives on interpretation and calibration. It is no wonder that producers are often confused or suspicious about the use of soil testing to predict fertilizer needs.

About 92% of all K fertilizer used in the USA is applied in states east of 95°W longitude (USDA, 1984), as expected from the distribution of K-responsive soils (Fig. 8-1). An average rate of only 4.3 kg of K ha⁻¹ (total K use divided by cropland area) was applied to cropland in the western states in 1982, in contrast to average rates > 50 kg ha⁻¹ in 18 of the 31 eastern states. Greatest average application rates were in Hawaii (288 kg of K ha⁻¹), followed by Florida at 159 kg of K ha⁻¹. Obviously, actual application rates vary with crop, soil, and management conditions.

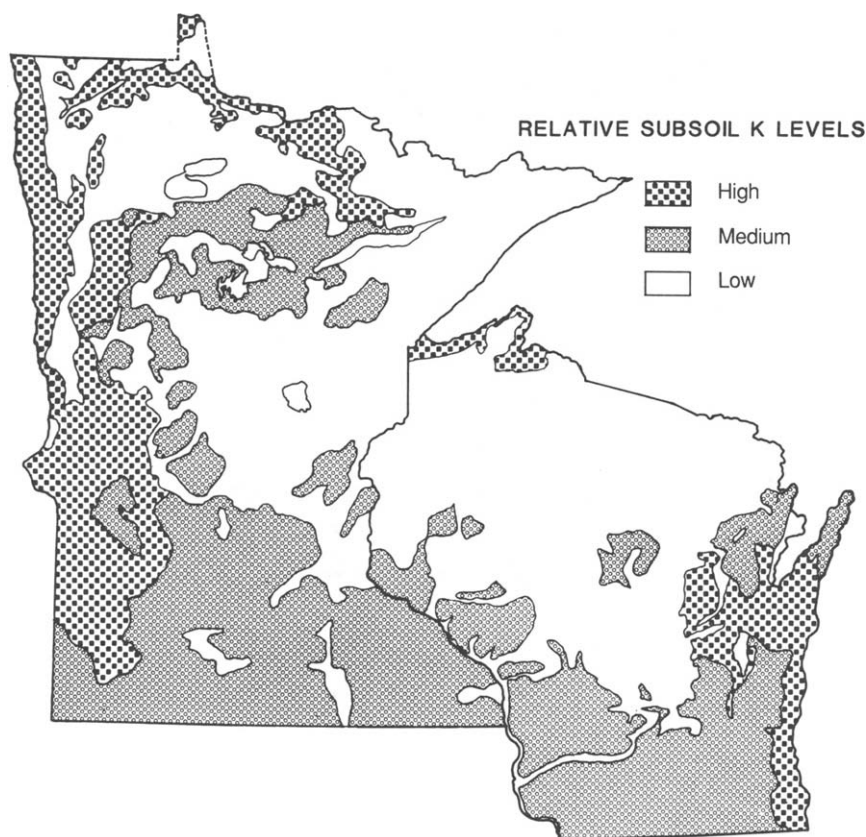


Fig. 8-16. Subsoil K status in Minnesota and Wisconsin. (Adapted from Kelling et al., 1981; and Rehm et al., 1985.)

The impact of subsoil K availability on crop yields has been alternately emphasized and disputed over the years. Seven public laboratories currently modify their recommendations with subsoil K fertility indexes, and a few others are conducting or contemplating further research. An example of subsoil K maps is presented in Fig. 8-16. Subsoil K status maps are usually based on standard exchangeable K analysis of dried samples acquired through extensive sampling of representative soil profiles. This approach could be questioned, because of the variable and often large changes in exchangeable K which occur upon air drying. Some laboratories predict K availability through use of other subsoil characteristics, such as depth, texture, bulk density, and average moisture status.

Although the use of subsoil K-fertility levels to modify K-fertilizer recommendations in intensively managed agriculture is not widespread, it is recognized as being important in many situations. Lack of crop yield response on some sandy Paleudults on the Coastal Plains and Timberlands areas of the southeastern USA and Texas has been reported because of an available supply of subsoil K (Yuan et al., 1976; Hons et al., 1976; Sparks et al., 1980; Woodruff & Parks, 1980). The Fertility Capability Classification System has a modifier, k, which is used to designate soils where K-supplying power is low (Sanchez et al., 1982).

Recent research in Montana has demonstrated that soil characteristics, such as mean annual soil temperature at 50 cm, moist consistence of the Ap horizon, moist and dry consistence of the B horizon, and the clay content of calcic horizons, can be used to identify sites and soils where a response to K can be expected (Schaff & Skogley, 1982b). These characteristics are related to the rate of K diffusion in the soil.

Reasonable success has been achieved in predicting subsoil K-availability indexes with other characteristics, such as clay content, which are typically included in Soil Survey information databases (Aighewi, 1988). These equations cannot be extrapolated beyond the region in which they were developed. It is unlikely that the size of one pool of soil K can be successfully predicted by another, because the relationship among K pools is not consistent in different soils (Fig. 8-17). Climatic factors are extremely influential in the response actually observed in the field, because soil moisture content and temperature greatly affect K diffusion (Schaff & Skogley, 1982a). Clearly, using inherent soil factors alone will not result in consistent predictions of K availability to crops.

B. Calcium

The major areas of concern for Ca supply to plants are in highly leached, acid soils and in soils where excessive levels of other cations such as K^+ , Na^+ , or NH_4^+ salts have been used, or where Mg in serpentine soils inhibits Ca uptake by plants. In sufficiently acid soils, Ca is primarily supplied as limestone to alleviate actual or potential phytotoxicities of Al^{3+} , Fe^{2+} , Mn^{2+} , and H^+ . Only in the absence of toxic amounts of these ions can one determine the need for Ca (Doll & Lucas, 1973). Melsted (1953) observed

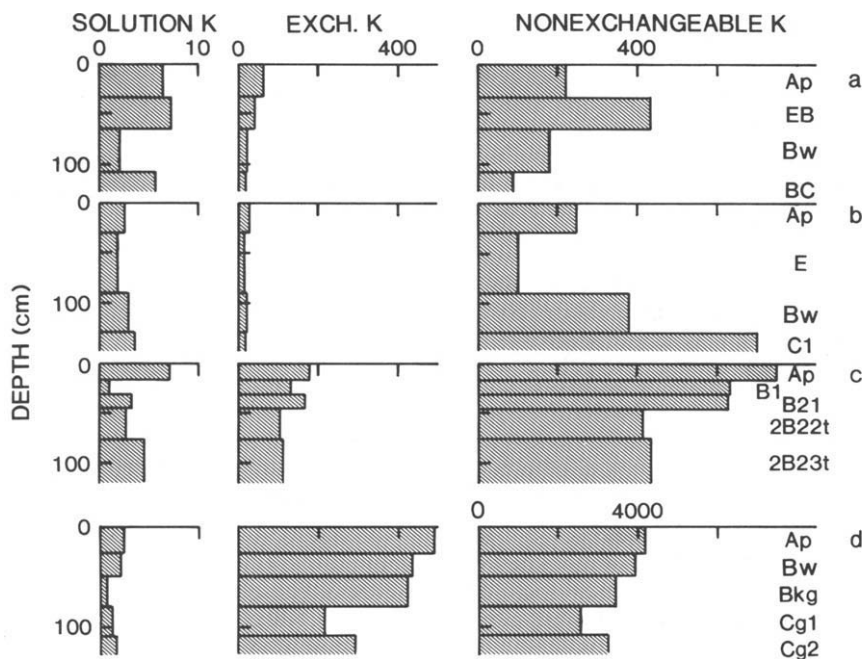


Fig. 8-17. Relationship between genetic horizon and various "pools" of soil K (all in mg kg^{-1}) for four Minnesota soils: (a) Entic Haploboroll; (b) Alfic Udipsamment; (c) Aquollic Hapludalf; and (d) Vertic Haplaquoll (I.T. Aigheui and M.P. Russelle, 1988, unpublished data). Note change in scale for nonexchangeable K for soil d.

Ca-deficiency symptoms on plants growing in soils having pH values below 4.5 and containing $< 400 \text{ mg Ca kg}^{-1}$. Many crops will respond to Ca applications when the degree of Ca saturation of the exchange capacity falls below 25%. Soybean was reported to suffer Ca deficiency at Ca saturations of 20% or less, while sugarcane in Hawaii grew normally with 12% Ca saturation in volcanic soils (Tisdale et al., 1985). Kaolinitic clays are able to satisfy the Ca requirements of most plants at lower saturation percentages than montmorillonite, which requires a Ca saturation of 70% or more before this element is released in sufficient supply to growing plants.

Although most suggestions are for application of Ca as limestone to correct the soil pH, nearly all laboratories maintain ratings of extractable Ca. Calcium levels at which crops are no longer expected to respond to Ca application vary among laboratories and soil types, and range from 250 mg kg^{-1} in Wisconsin sandy soils to 500 mg kg^{-1} in Wisconsin silty clay soils. Several states use the Ca saturation percentage of the soil CEC to determine adequate Ca availability. Maine defines 75% Ca saturation as adequate.

Most laboratories use the same extractant for Ca as is used for K (Fig. 8-8). The most widely accepted Ca extraction method appears to be 1 M ammonium acetate at pH 7 for soils of the USA and Canada. Concentrations of Ca extracted by this method and especially by any acidic extracting solution, will include Ca solubilized from native or applied and unreacted

CaCO₃. Extractable Ca would be a more appropriate term to use than exchangeable, especially when acidic extractants are used.

C. Magnesium

Attempts to correlate extraction of soil Mg with crop response rarely include evaluation of subsoil Mg. Elimination of plant access to subsoil Mg is one reason why greenhouse research on soil Mg and crop response is usually more successful than field research in producing statistically significant correlations. Soil material used in greenhouse research is normally collected from the soil surface and is only part of the rooting medium to which plants have access in the field. Significant exchangeable Ca and Mg movement into subsoil to depths of at least 45 cm because of limestone application on acid sandy soils was reported by Haby et al. (1979) and Messick et al. (1984). Acid, sandy Alfisols and Ultisols in which plants might be expected to respond to Mg application, often contain an argillic horizon or zone of clay accumulation. In addition, certain of these soils contain interstratified mica and vermiculite in the fine silt and clay fractions (Hons et al., 1976; Yuan et al., 1976). In the micaceous minerals, Mg can exist in the interlayer positions and can partially substitute for Al in the octahedral layer. This Mg would be considered nonexchangeable. Rice and Kamprath (1968) reported that nonexchangeable Mg was readily soluble in dilute acid extractants and may be important for plant growth. A large part of the Mg taken up by corn plants in four of the five soils they studied was from nonexchangeable forms (Fig. 8-5). They hypothesized that a microzone of H⁺ ions exists around plant roots. Since the sandy soils used in their study did not have a high buffer capacity, the H⁺ ions exchanged from the roots could be quite effective in releasing Mg from the nonexchangeable form. This mechanism might be responsible for many Coastal Plains and other sandy, acid soils not responding to Mg fertilization even though the exchangeable Mg content in the surface is low. This concept was verified by Christenson and Doll (1973), but would depend to a large degree on the ratio of anions to cations absorbed by the plant, as this ratio affects rhizosphere pH.

Two main methods of reporting soil test Mg levels on which to base fertilizer recommendations for Mg are percent saturation of the soil CEC and exchangeable Mg. Fox and Piekielek (1984) indicated exchangeable Mg was highly correlated ($r = 0.99$) with Mg as a percent saturation of the soil CEC. The general consensus appears to be that 5% Mg saturation of the soil CEC is adequate for optimum yields of most crops. For those crops that require a higher concentration of basic cations, such as alfalfa, and for crops such as corn silage and cool-season forages needing higher concentrations of Mg to prevent hypomagnesaemia in ruminant animals, 10% Mg saturation of the soil CEC is suggested to maintain the Mg concentration in the dry matter at 2 g kg⁻¹ or above. Where acidified soil extractants are used, such as pH 3, *M* ammonium acetate used in Maine, 15% is the Mg saturation percentage above which Mg application is no longer considered necessary for increased yields. Lancaster (1958) reported that the probability of

cotton response to Mg application on heavy clay soils was excellent at 3% Mg saturation of the soil CEC and no response was expected above 6.4% saturation.

The sum of exchangeable cations by routine soil extraction includes soluble and soil solution cations and may not represent the total extraction of the exchange complex. Therefore, the actual soil CEC rather than the sum of exchangeable cations should be used to be most accurate when using percent Mg saturation to predict Mg requirements. Until recently, determination of soil CEC was not adapted as a routine analytical procedure suitable for use in a soil-testing laboratory. Begheyn (1987) has developed a single step CEC analysis procedure that may meet the rapid and routine requirements of soil-testing laboratories.

Fox and Piekielek (1984) reported that the exchangeable Mg level recommended for agronomic crop production by different soil-testing services ranged from 25 to 180 mg kg⁻¹. Research on various crops and soils indicated a range of critical levels for soil exchangeable Mg that varied from about 7 to 35 mg kg⁻¹, depending upon subsoil Mg supply, soil K and Ca content, and fertilizer NH₄ application. Respondents to our survey indicated that the range of exchangeable Mg above which fertilizer Mg is no longer recommended varied from 25 to 60 mg kg⁻¹. This range varied from 30 mg kg⁻¹ for sandy soils to 50 mg kg⁻¹ for silts and clays, and was highest in the Piedmont soils.

According to Doll and Lucas (1973), guidelines established by the advisory workers in the United Kingdom (N.A.A.S., 1968) agree fairly well with North American observations. These levels of exchangeable Mg and interpretations are as follows:

1. 0–25 mg of Mg kg⁻¹: Deficiency symptoms general in most field crops, vegetables, fruit, and glasshouse crops. Magnesium is certainly advised.
2. 26–50 mg of Mg kg⁻¹: Deficiency expected in sugarbeet, potato, kale (*Brassica oleraceae* DC.), fruit, and glasshouse crops. Magnesium is advised except for cereal crops.
3. 51 to 100 mg of Mg kg⁻¹: Absolute deficiency is not likely in field and most vegetable crops. If symptoms occurred, they were likely induced by other factors such as wide K to Mg ratio in the soil. However, Mg is suggested for fruit, glasshouse crops, and grassland crops. Before recommending Mg for grassland, the economics of the treatment should be compared with the cost of direct feeding of magnesia (MgO) to animals.
4. 101 to 175 mg of Mg kg⁻¹: Standard Mg treatment should be given to glasshouse crops [tomato, cucumber (*Cucumis sativus* L.), pepper (*Capsicum annuum* L. var. *annuum*)]. Treatment of grassland should be required where hypomagnesaemia in animals has been confirmed.
5. 176 to 250 mg of Mg kg⁻¹: Magnesium suggested only for glasshouse crops.

V. PROGNOSIS

Economic and environmental concerns mandate that fertilizer recommendations be as accurate and precise as possible. In the short term, nutrient availability indexes of extractable K and Ca and exchangeable Mg will continue to be used despite their shortcomings. Improved methods will be devised as the mechanistic relationships among soil, plant, and climatic conditions are resolved and true phytoavailability is understood. Recommendations of nutrient inputs will remain imprecise because of the unpredictability of weather, and therefore plant growth. Fundamental advances in understanding nutrient supply, uptake, and analytical methodology made since the second edition of this book in 1973 provide a promising basis for future research.

Development and validation of new methodologies and approaches to soil testing and fertilizer recommendations are time- and resource-consuming. Recognized inefficiencies in current methods make it imperative that this work continue and increase. The excellent cooperation among many public and private soil-testing laboratories in improving soil test correlations, evaluating new extraction techniques, and in sharing discoveries and data should be encouraged, recognized, and supported by administrators. Finally, the extension of this knowledge to producers and supporting industries is crucial—both the potentials and limitations of testing technologies must be understood.

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Chapter 9

Testing Soils for Copper, Iron, Manganese, and Zinc¹

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Recognition that Cu, Fe, Mn, and Zn are essential for plant growth and that Cu, Fe, Mn, and Zn deficiencies occur in the field preceded the development of soil tests for the micronutrient cations. The essentiality of Fe for plant growth was proven in 1844 by Gris (Bonner & Galston, 1952) and that of Mn in 1905 by Bertrand (Stout, 1956). In 1914, Maze provided the evidence that Zn was needed by plants and, in 1928, Sommer and Lipman demonstrated the plant requirement for Cu (Stout, 1956). The criterion for essentiality was based on the inability of plants to complete their life cycles under conditions of insufficient Cu, Fe, Mn, or Zn.

After establishment of the essentiality of Cu, Fe, Mn, and Zn, it was a normal progression to evaluate whether lack of these elements caused abnormal plant growth on problem soils. These micronutrient deficiencies were first identified under field conditions in horticultural crops. Copper deficiency of citrus, or "dieback," and Mn deficiency of tomato (*Lycopersicon esculentum* Mill.) were identified in Florida by Grossenbacher (1916) and Skinner and Ruprecht (1930), respectively. Deficiencies of Fe (Thomas & Haas, 1928) and Zn (Chandler et al., 1932) were diagnosed in Californian citrus. Thereafter, these deficiencies were confirmed in agronomic crops under field conditions. Copper and Mn deficiencies of oat (*Avena sativa* L.) plants were confirmed in Wales (Davies & Jones, 1931) and Florida (Harris, 1947), respectively. A chlorotic condition of sorghum [*Sorghum bicolor* (L.) Moench], which limited grain yields on the Southern Great Plains, was diagnosed as Fe deficiency (Myers & Johnson, 1933). Barnette et al. (1936) reported that Zn application as ZnSO₄ increased corn (*Zea mays* L.) grain yield and that

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application of superphosphate with ZnSO_4 rendered the Zn less efficient in correction of the "white bud" in corn.

The need for laboratory procedures to identify soils with inadequate amounts of Cu, Fe, Mn, and Zn for plants became apparent in the 1930s as these deficiencies were confirmed under field conditions. It was recognized early that the plant availabilities of Cu, Fe, Mn, and Zn were governed by soil properties and, therefore, that the total concentrations of these elements in soils would not serve as a suitable indicator of plant-available Cu (Mulder, 1939), Fe and Mn (Mann, 1930), or Zn (Alben & Boggs, 1936). An exception was organic soils with low total concentrations and concomitant low availabilities of these micronutrient cations.

The inconsistent relationship between the micronutrient cation availabilities and total concentrations in most soils led to the conclusion that availability tests for these elements should be based on portions extracted from soil (Hibbard, 1940). The initial soil tests were based on amounts of the micronutrient cations extracted from soils by inorganic reagents or bioassay procedures with the fungus, *Aspergillus niger*. Immediately, problems were encountered on the choice of extractant and the methodology for determining the low concentrations of metals extracted from soil (Hibbard, 1940).

Extraction and determination of low amounts of Cu and Zn were accomplished with an *A. niger* bioassay. Initial attempts to use the bioassay for estimation of plant-available Cu and Zn in soil were unsuccessful. The problem encountered was the nutrient solution contamination supplied the low Cu and Zn requirements for *A. niger* and, consequently, that standard curves were unobtainable. Use of a nutrient solution purification procedure developed by Steinberg (1919), which entailed metal adsorption on CaCO_3 added to nutrient solution and separation of the liquid and solid phases by decantation, led to successful use of the bioassay for Cu (Mulder, 1939) and Zn (Bould et al., 1949). Mulder (1939) estimated available Cu in soil by comparing *A. niger* spore color on soil cultures and a series of cultures with increasing increments of Cu. Severe Cu deficiency of oat plants occurred on soils with a level of $<0.6 \text{ mg of Cu kg}^{-1}$. Bould et al. (1949) estimated available Zn in soil by comparing the dry weight of *A. niger* tissue on soil cultures and a series of cultures with increasing increments of Zn. They confirmed the occurrence of Zn deficiency in fruit trees by this bioassay method.

Interest in the *A. niger* bioassay for evaluation of available Cu and Zn waned with the development of improved analytical methods for micronutrient cation determination. Furthermore, the bioassay method was not completely adaptable to the soil test requirements, which were summarized by Bray (1948) as follows:

1. The extraction solution and procedure should solubilize a proportionate part of the available forms of a nutrient in soils with variable properties.
2. The amount of the nutrient in the extract should be measurable with reasonable accuracy and speed.
3. The amount extracted should be correlated with crop response to that nutrient under various conditions.

The long incubation period for the bioassay negates its adaptability as a routine soil test procedure. In addition, the procedure does not meet the current goal of simultaneous extraction and determination of Cu, Fe, Mn, and Zn to allow rapid conveyance of the soil test results to crop producers at a reasonable cost (Havlin & Soltanpour, 1981; Selvarajah et al., 1982). Hence, the *A. niger* bioassay will not receive further comment, and the chemical extractants, which are adaptable to the soil test requirements, will receive emphasis herein.

The purpose of this chapter, which is a revision of the one written by Viets and Lindsay (1973), is to review the current status of soil testing for Cu, Fe, Mn, and Zn. Advances in simultaneous extraction and determination of the micronutrient cations as well as improvements in soil test calibration data warrant this revision. Portions of this subject are covered in other chapters (Cox & Kamprath, 1972; Viets & Lindsay, 1973; Mortvedt, 1977; Knezek & Ellis, 1980; Sillanpaa, 1982; Lindsay & Cox, 1985). It is our goal to minimize redundancy with the aforementioned chapters, but for clarity's sake, some overlap is unavoidable.

I. PROCEDURES FOR SOIL TEST DEVELOPMENT

The three sequential steps generally followed to develop micronutrient cation soil tests are extractant selection, greenhouse evaluation, and field calibration. The first step is to select an extractant that will solubilize a proportionate part of labile forms of the micronutrient cations from different soils. The second step is to evaluate if amounts of cations extracted are related to the quantities absorbed by plants from the different soils. To decrease cost and to obtain data more quickly, this step commonly is completed in the greenhouse rather than in the field. It is assumed that, if the amounts of extractable micronutrient cations are unrelated to crop response to their application under controlled greenhouse conditions, then a suitable relationship will not be obtainable in harsher field environments. The third step, field calibration of a soil extractant, is conducted if a suitable relationship is established during the greenhouse evaluation.

Field calibration of a micronutrient cation soil test commonly entails the determination of a critical level, i.e., the soil test value that separates soils into responsive and nonresponsive categories. The critical level is based on yield response to application of the micronutrient under field conditions. Another method used in field calibration research is to determine the insufficient, sufficient, and the transitional zone between insufficient and sufficient levels of the available micronutrient cations in soils. The small yield increases from micronutrient cation applications on many soils led to difficulty in use of the latter method. Statistical procedures using the interaction chi-square technique could be used to identify the boundaries of the transitional zone (Keisling & Mullinix, 1979; Havlin & Soltanpour, 1982).

Economically, it would be desirable to calibrate micronutrient cation soil tests under greenhouse conditions. There are, however, several reasons

why critical levels determined for micronutrient cation soil tests in the greenhouse may not be applicable to field conditions. Differences in cation uptake occur in greenhouse as compared with field for the following reasons:

1. Use of higher rates of NH_4^+ fertilizer causes lower levels of pH in pots than in field soils.
2. Use of larger amounts of nutrients in pots leads to higher soluble-salt levels.
3. Greater root-to-soil contact occurs from plant root confinement in pots.
4. Abnormal light, relative humidity, and moisture regimes occur in the greenhouse (Logan & Chaney, 1983; Mortvedt, 1977).

Quite often nutrients are supplied at rates inadequate to obtain maximum plant growth under greenhouse conditions (Terman, 1974). Such insufficiency contributes to variations in plant concentration, uptake, and yield response to micronutrient cation application and, hence, to an unacceptable greenhouse evaluation of a soil test. Also, it is unacceptable to extrapolate critical levels from the vegetative growth stage in the greenhouse to the maturity growth stage under field conditions.

Greenhouse soil tests are commonly conducted with soil from the Ap horizon, whereas in the field, plants absorb nutrients from the Ap and lower horizons. This difference leads to the anomaly illustrated in the research by Iyengar et al. (1981). Zinc application increased the dry weight of corn grown on a Dunmore silt loam (clayey, kaolinitic, mesic Typic Paleudult) in the greenhouse, but not in the field where roots absorbed some Zn from acidic soil below the Ap horizon. In other research, Cu application increased tick trefoil (*Desmodium uncinatum*) and white clover (*Trifolium repens* L.) yields under greenhouse conditions, but only white clover yield was increased by Cu application in the field (Andrew & Thorne, 1962). The difference was attributed to the deep root system of tick trefoil as compared with the shallow root system of white clover. Copper absorption from subsoil by tick trefoil negated a yield response to Cu application.

It is desirable to base the greenhouse evaluation step on increases in plant dry weights from application of the micronutrient cations. Although growth responses to Cu, Fe, and Zn application commonly are obtained with plants grown in the greenhouse, growth responses to Mn application are not always possible. For example, Tierney (1981) collected eight soils from fields where soybean [*Glycine max* (L.) Merr.] plants were severely Mn deficient, but did not obtain a growth response to Mn application in the greenhouse. Unavoidable changes in $\text{pe} + \text{pH}$ in pots increased Mn availability and, thus, negated soybean yield response to Mn application in the greenhouse. It is for this reason that steps two and three frequently are combined and completed under field conditions for development of a Mn soil test.

In some cases, critical micronutrient cation soil test values obtained in greenhouse research have been used as guides to evaluate whether micronutrient cation deficiencies would occur under field conditions. This use of

greenhouse critical levels is open to criticism. Nevertheless, this approach has been necessary on an interim basis during completion of the field calibration research for a soil test.

II. MICRONUTRIENT CATION FORMS SOLUBILIZED BY VARIOUS EXTRACTANTS

Ideally, extractants for Cu, Fe, Mn, and Zn soil tests should be selected from the standpoint of solubilization of a proportionate part of the labile forms in different soils. This selection requires knowledge of the labile micronutrient cation forms in soil. A labile ion is an ion in soil solution or one in the solid phase that may exchange with the same kind of ion in soil solution.

A. Micronutrient Cation Forms in Soils

The micronutrient cations exist in the following forms in soils: (i) as free and complexed ions in soil solution, (ii) as nonspecifically and specifically adsorbed cations, (iii) as ions occluded mainly in soil carbonates and hydrous oxides, (iv) in biological residues and living organisms, (v) in the lattice structure of primary and secondary minerals, and (vi) as precipitates (McLaren & Crawford, 1973; Sims & Patrick, 1978; Lindsay, 1979; Iyengar et al., 1981). The solubilities of Fe and Mn hydrous oxides are sufficiently low that precipitation of these compounds commonly occurs even in slightly acid soils (Lindsay, 1979). In contrast, Cu and Zn hydrous oxides would be unstable in acid soils except where unusually high activities of the two micronutrients occur in soil solution.

Nonspecifically adsorbed Cu^{2+} , Fe^{2+} , Mn^{2+} , and Zn^{2+} occur in soils from formation of an outer-sphere complex with a functional group and the cation, i.e., through bond formation by electrostatic interaction (Sposito, 1981). This bond formation is exemplified by the attraction between these cations and the charge arising from isomorphous substitution in phyllosilicates (Sposito, 1981) or between Mn^{2+} and a functional group of organic matter (Gamble et al., 1976). A nonspecifically adsorbed cation usually is referred to as an exchangeable cation.

Specific adsorption refers to formation of an inner-sphere complex between a micronutrient cation and functional group of soil components (Sposito, 1981). In soils, Cu, Fe, Mn, and Zn cations would be specifically adsorbed by carbonates, hydrous oxides of Al, Fe, and Mn, soil organic matter, and phyllosilicates (Udo et al., 1970; Schnitzer, 1978; Kabata-Pendias & Pendias, 1985).

Occlusion is the formation of a second layer of adsorbed ions over an adsorbed ion such that the originally adsorbed ion no longer is in contact with soil solution and, therefore, cannot dissociate into soil solution. This occlusion occurs as a layer of Al, Fe, or Mn hydroxide precipitates over micronutrient cations, which are complexed by organic matter or adsorbed on carbonate, hydrous oxide, and phyllosilicate surfaces.

Labile micronutrient cations consist of free and complexed cations in soil solution, which provide the intensity of soil to supply nutrients to plants, and the nonspecifically and specifically adsorbed cations, which provide the soil with the capacity to replenish these cations into soil solution. Labile forms are the plant-available sources of the cations. Thus, a soil test extractant should solubilize the labile forms for estimates of plant availability.

Labile micronutrient cations are in metastable equilibria with nonlabile forms in soils. Therefore, portions of labile forms revert to nonlabile forms with time and, conversely, portions of the nonlabile forms revert to the labile forms upon weathering. It is recognized that the labile forms of a cation in soil change rapidly under dynamic soil conditions such as fluctuations in pH . An inherent limitation of soil micronutrient cation soil tests is the attempt to extract labile forms from a dry or moist soil sample, which may differ from labile forms in field soil from the same location during a growing season.

B. Forms Solubilized by Various Extractants

The many soil test extractants that have been developed for solubilizing micronutrient cations fall within four categories: chelating agents, inorganic acids, neutral salts, and reducing agents (Table 9-1). Neutral salt solutions extract nonspecifically adsorbed micronutrient cations that are in a metastable equilibrium with soil solution. The cation in the neutral salt may displace hydrated Al^{3+} that could hydrolyze in soil solution to produce H_3O^+ . The H_3O^+ ions then displace specifically adsorbed micronutrient cations by dissociating cation-organic matter complexes and by partially dissolving carbonate and hydrous oxide surfaces. Overall, the amounts of micronutrient cations solubilized with neutral salts are much lower than the quantities extracted with chelating agents, reducing agents, and strong and weak acids (McLaren & Crawford, 1973; Viets & Lindsay, 1973; Sims & Patrick, 1978; Lindsay, 1979; Iyengar et al., 1981).

The quantities of micronutrient cations solubilized from soil by extraction with strong or weak acid depend on the amount of H_3O^+ neutralization in the soil-extraction solution mixture and on the extraction time. A solution with a very low acid concentration (activity) would extract small amounts of micronutrient cations from about the same sources as would neutral salts; proportionally higher amounts would be extracted with increases in acid concentration and extraction time. Extraction with 0.1 M HCl commonly has been used for estimation of plant-available Zn. This extractant would solubilize micronutrient cations by dissociating cation-organic matter complexes, by displacing specifically adsorbed cations from carbonate, hydrous oxide, and phyllosilicate surfaces, and by releasing nonlabile occluded and precipitated cations during partial acid decomposition of minerals. The acid also would release octahedrally coordinated Cu, Fe, Mn, and Zn from phyllosilicates as the exposed mineral surfaces undergo acid attack. The amounts released from phyllosilicates would vary with soil mineralogy because some phyllosilicates, e.g., kaolinite, are more resistant to acid attack than are others (Lindsay, 1979).

Table 9-1. Critical levels for Cu, Fe, Mn, and Zn soil tests based on either greenhouse evaluation or field calibration research.

Research	Crop(s)	Soil(s)	Extractant	Critical level	Reference
Field Greenhouse	Barley and oat Rice Corn, soybean, and wheat	30 soils, pH 5.2-6.7 16 soils, pH 5.5-8.5 15 noncalcareous soils	<u>Cu soil tests</u>		Reith, 1968 Ponnampetuma et al., 1981 Makarim & Cox, 1983
			0.05 <i>M</i> EDTA	1.1 mg Cu kg ⁻¹	
			0.05 <i>M</i> HCl	0.1 mg Cu kg ⁻¹	
			Mehlich-I	0.26 mg Cu dm ⁻³	
Field	Soybean and wheat	7 noncalcareous soils	Mehlich-Bowling	0.62 mg Cu dm ⁻³	Makarim & Cox, 1983
			NH ₄ HCO ₃ -DTPA	0.53 mg Cu dm ⁻³	
			Mehlich-III	0.37 mg Cu dm ⁻³	
			Mehlich-Bowling	0.70 mg Cu dm ⁻³	
Greenhouse	Sorghum Sorghum	35 calcareous soils 40 soils, 35 calcareous, and 5 noncalcareous	<u>Fe soil tests</u>		Lindsay & Norvell, 1978 Havlin & Soltanpour, 1981
			DTPA-TEA	4.5 mg Fe kg ⁻¹	
			NH ₄ HCO ₃ -DTPA	4.8 mg Fe kg ⁻¹	
			DTPA-TEA	4.8 mg Fe kg ⁻¹	
Field	Soybean	25 soils, pH 5.7-7.4	<u>Mn soil tests</u>		Hoff & Mederski, 1958
			0.033 <i>M</i> H ₃ PO ₄	20 mg Mn kg ⁻¹	
			1.0 <i>M</i> NH ₄ H ₂ PO ₄	20 mg Mn kg ⁻¹	
			Alcoholic hydroquinone	63 mg Mn kg ⁻¹	
Field	Oat	25 soils, pH 6.7-7.7	0.033 <i>M</i> H ₃ PO ₄	20 mg Mn kg ⁻¹	Hammes & Berger, 1960a
			1.5 <i>M</i> NH ₄ H ₂ PO ₄	20 mg Mn kg ⁻¹	
			0.05 <i>M</i> EDTA	50 mg Mn kg ⁻¹	
			Hydroquinone-NH ₄ OAc	65 mg Mn kg ⁻¹	
Field	Soybean	17 soils, pH 5.2-7.1	Mehlich-I	pH variable-5.2 mg Mn kg ⁻¹ at pH 6.0	Cox, 1968
			Mehlich-I	2.6 mg Mn kg ⁻¹	
			DTPA-TEA	0.22 mg Mn kg ⁻¹	
			NH ₄ HCO ₃ -DTPA	0.40 mg Mn kg ⁻¹	
Field	Corn	One sandy soil, pH 6.4-7.2	Mehlich-III	pH variable-3.0 mg Mn dm ⁻³ at pH 6.4	Mascagni & Cox, 1984

(continued on next page)

Table 9-1. Continued.

Research	Crop(s)	Soil(s)	Extractant	Critical level	Reference
<u>Mn soil tests</u>					
Field	Soybean	30 soils, pH 5.1-6.9	Mehlich-I	pH variable-4.6 mg Mn kg ⁻¹ at pH 6.0	Gettier et al., 1985c
Field	Soybean	38 soils, pH 5.5-7.1	Mehlich-I	pH variable-4.7 mg Mn kg ⁻¹ at pH 6.0, 3.9 mg Mn dm ⁻³ at pH 6.0	Mascagni & Cox, 1985
			Mehlich-III		
<u>Zn soil tests</u>					
Field	Corn	15 soils, pH 4.7-6.2	0.1 M HCl	1.0 mg Zn kg ⁻¹	Wear & Sommer, 1948
Greenhouse	Corn	42 soils, neutral and calcareous	EDTA-(NH ₄) ₂ CO ₃	1.4 mg Zn kg ⁻¹	Trierweiler & Lindsay, 1969
Greenhouse	Sweet corn	92 soils, most with a pH of 7.0-8.2	Dithizone-NH ₄ OAc	0.95 mg Zn kg ⁻¹	
Field	Corn	10 soils, pH 5.4-7.2	DTPA-TEA	0.5 mg Zn kg ⁻¹	Brown et al., 1971
Field	Corn	34 soils, pH 4.7-8.3	Dithizone-NH ₄ OAc	0.55 mg Zn kg ⁻¹	
			EDTA-(NH ₄) ₂ CO ₃	0.8 mg Zn kg ⁻¹	Alley et al., 1972;
			Mehlich-I	0.8 mg Zn kg ⁻¹	Cox & Wear, 1977
			0.1 M HCl	1.4 mg Zn kg ⁻¹	
			DTPA-TEA	0.5 mg Zn kg ⁻¹	
			DTPA-TEA	0.8 mg Zn kg ⁻¹	Lindsay & Norvell, 1978
Greenhouse	Corn	42 calcareous and non- calcareous soils	DTPA-TEA	0.6 mg Zn kg ⁻¹	Lindsay & Norvell, 1978
Greenhouse	Sorghum	35 calcareous and non- calcareous	DTPA-TEA		
Greenhouse	Green gram	22 soils, pH 7.0-8.7	DTPA-TEA	0.48 mg Zn kg ⁻¹	Gupta & Mittal, 1981
			EDTA-(NH ₄) ₂ CO ₃	0.70 mg Zn kg ⁻¹	
			0.1 M HCl	2.2 mg Zn kg ⁻¹	
Greenhouse	Corn	40 soils, 35 calcareous and 5 noncalcareous	NH ₄ HCO ₃ -DTPA	0.9 mg Zn kg ⁻¹	Havlin & Soltanpour, 1981
Greenhouse	Rice	22 soils, pH 5.5-8.5	DTPA-TEA	0.7 mg Zn kg ⁻¹	
Greenhouse	Rice	46 soils, pH 8.8-10.7	0.05 M HCl	1.0 mg Zn kg ⁻¹	Ponnamperuma et al., 1981
			DTPA-TEA	0.86 mg Zn kg ⁻¹	Singh & Takkar, 1981
			EDTA-(NH ₄) ₂ CO ₃	1.00 mg Zn kg ⁻¹	

The noncrystalline Al, Fe, and Mn hydrous oxides are more susceptible to acid attack with release of occluded, adsorbed, and precipitated micronutrient cations than the crystalline hydrous oxides of these elements. This susceptibility reflects the greater surface area of the noncrystalline compounds. At sufficiently low levels of extraction solution pH, specifically adsorbed and occluded micronutrient cations are released as crystalline primary minerals such as gibbsite, pyrolusite, and strengite undergo partial acid decomposition. Because acids extract portions of nonlabile metal cations, either soil pH or titratable alkalinity often is used in conjunction with an acid extractable cation to improve the prediction of the plant-available cation status in soil (Nelson et al., 1959; Cox, 1968).

The reducing agent, hydroquinone, has been used to solubilize Mn in the development of a Mn soil test. Leeper (1934) extracted easily reducible Mn with a solution of 1.0 *M* NH₄OAc and 0.05% hydroquinone to estimate available soil Mn. The hydroquinone reduces a portion of the Mn in noncrystalline Mn hydrous oxides and thereby liberates Mn into solution (Sherman et al., 1942). There could be some readsorption of Mn by soil at the pH of this soil-extraction solution mixture.

The diethylenetriaminepentaacetic acid-triethanolamine (DTPA-TEA) (0.005 *M* DTPA; 0.01 *M* CaCl₂; 0.1 *M* TEA, buffered at pH 7.3) soil test procedure is among the more widely used techniques to identify soils with inadequate levels of available Cu, Fe, Mn, and Zn. Lindsay and Norvell (1978) described the theoretical basis for the procedure. The DTPA molecules form water-soluble complexes with free metal cations and, thereby, decrease the cation activities in solution. In response, cations desorb from soil surfaces or dissolve from labile solid phases to replenish solution cations. Amounts of chelated cations that accumulate in solution during the extraction are a function of both cation activity in the soil solution (intensity factor) and the ability of the soil to replenish those cations (capacity factor). Plant uptake of a micronutrient increases with increases in soil solution cations and the capacity of soil solid phases to replenish cations depleted from soil solution (Lindsay, 1979).

The chelating agent, DTPA, was selected for the soil test because it had the most favorable combination of stability constants for simultaneous complexation of Cu, Fe, Mn, and Zn (Lindsay & Norvell, 1978). Since Fe and Zn deficiencies are prevalent on calcareous soils, the extractant was designed to avoid excessive dissolution of CaCO₃ with the release of occluded micronutrient cations, which normally are not available for absorption by plant roots. Excessive dissolution was prevented by inclusion of soluble Ca²⁺ as CaCl₂ in the extraction solution and by buffering the solution at pH 7.3 with TEA.

C. Effects of Soil Sample Preparation

Amounts of extractable Cu, Fe, Mn, and Zn in soils are affected by sample drying, grinding force and time, and quantity of sample being ground. The effects of sample preparation procedures on extractable Cu, Fe, Mn,

and Zn vary among soils and laboratories. It would be desirable to standardize sample preparation procedures to ensure that comparable levels of extractable Cu, Fe, Mn, and Zn are obtained in different laboratories (Soltanpour et al., 1976).

Drying moist samples of diverse United Kingdom soils decreased the concentrations of easily reducible Mn and increased water soluble plus exchangeable Mn (Goldberg & Smith, 1984). Explanations for the decrease in easily reducible Mn were as follows: (i) dehydration of Mn hydrous oxides, (ii) reduction of Mn in hydrous oxides by organic matter, and (iii) alteration of functional groups that tightly complex Mn. Hammes and Berger (1960b) attributed Mn release on drying of moist soil to chemical oxidation of the organic component of organo-Mn complexes with release of Mn^{2+} to labile water soluble and exchangeable forms.

Drying moist samples affects the amounts of micronutrient cations extracted from soils by currently used soil tests. Air drying increased Mn extracted by 0.033 *M* H_3PO_4 from seven soils (Hammes & Berger, 1960b). Amounts of DTPA-TEA extractable micronutrient cations were increased by air-drying neutral and calcareous soil samples: two- to threefold for Fe and 1.3- to 1.5-fold for Cu, Mn, and Zn (Leggett & Argyle, 1983). The DTPA-TEA extractable Fe and Mn increased over the drying temperature range from 22 to 100°C, whereas DTPA-TEA extractable Cu and Zn levels changed only slightly over this temperature range. Similar temperature effects occurred for levels of extractable Cu, Fe, Mn, and Zn by the DTPA-TEA and NH_4HCO_3 -DTPA (1.0 *M* NH_4HCO_3 , 0.005 *M* DTPA, buffered at pH 7.6) procedures for two alkaline soils (Leggett & Argyle, 1983). Although inconvenient, it may be necessary to keep soil moist and to store moist samples under aerobic conditions prior to extraction to minimize changes in labile micronutrient cations (Bartlett & James, 1980).

Differences in grinding force and time as well as amounts of soil being ground cause variation in levels of DTPA-TEA extractable micronutrient cations (Soltanpour et al., 1976). As the amount of soil being ground was increased from 200 to 400 g, at a grinding force of 6.6 kg for either 30 or 120 s, there was a decrease in extractable Fe from two soils (Table 9-2). The extractable Zn in the soils was increased by a longer grinding time from 30 to 120 s and by an increase in grinding force from 3.2 to 6.6 kg. The magnitude of these Zn increases was much less than for Fe. An increase in grinding time increased the extractable Mn levels in the soils, whereas extractable Cu levels were unaffected by differences in grinding time.

The NH_4HCO_3 -DTPA procedure was developed for simultaneous extraction of micronutrient cations and macronutrients from neutral and alkaline soils (Soltanpour & Schwab, 1977). Equilibrium is not attained during the 15-min shaking period for the procedure and, therefore, any factor that affects the reaction rate between the NH_4HCO_3 -DTPA solution and soil changes the amounts of extractable Cu, Fe, Mn, and Zn (Soltanpour et al., 1979a). Soltanpour et al. (1979a) studied the effect of weight of soil being ground and grinding force and time on NH_4HCO_3 -DTPA extractable Cu, Fe, Mn, or Zn. An increase in weight of soil being ground decreased extract-

Table 9-2. Effect of sample size, grinding force, and grinding time on DTPA-TEA extractable Zn, Fe, Mn, and Cu for two soils (Soltanpour et al., 1976).

Micronutrient cation	200 g Soil				400 g Soil			
	3.2 kg force		6.6 kg force		3.2 kg force		6.6 kg force	
	30 s	120 s	30 s	120 s	30 s	120 s	30 s	120 s
	mg kg ⁻¹							
	Soil 1							
Zn*	0.25	0.39	0.32	0.66	0.26	0.39	0.28	0.50
Fe*	6.5	24.3	15.4	50.8	6.2	25.1	10.7	37.8
Mn†	5.5	7.0	6.3	8.9	5.9	7.2	6.0	8.2
Cu‡	0.76	0.71	0.73	0.76	0.76	0.73	0.62	0.76
	Soil 2							
Zn*	0.36	0.41	0.32	0.57	0.29	0.39	0.32	0.36
Fe*	10.0	21.1	14.0	44.8	7.6	16.3	10.9	19.1
Mn†	4.6	5.1	4.4	6.8	4.5	4.8	4.5	5.2
Cu‡	0.39	0.56	0.28	0.80	0.34	0.42	0.28	0.28

* Effects of size of soil sample, grinding time, and grinding force were significant at the 0.05 level. Interaction effect of force \times time was significant at the 0.10 level.

† Effect of time was significant at the 0.10 level.

‡ No significant effect.

able Fe slightly and did not affect levels of extractable Cu, Mn, and Zn. An increase in extractable Fe and Zn occurred with increases in both grinding force and time, but these grinding parameters did not affect levels of extractable Cu and Mn.

Effects of grinding parameters on extractable micronutrient cations vary with their forms in soils. Grinding to a smaller particle size increases the surface area of Fe hydroxides and oxides exposed to extraction solution and, hence, increases the extractability of Fe as well as occluded Cu, Mn, and Zn in the hydroxides and oxides (Severson et al., 1979; Soltanpour et al., 1979a). In contrast, grinding to smaller particle size has little effect on extractable cations in soil forms that are soluble in the extraction solution (Soltanpour et al., 1979a).

D. Effects of Extraction Parameters

Amounts of extractable Cu, Fe, Mn, and Zn are affected by concentrations of extraction solution components, extraction time, soil-extraction solution ratio, extraction temperature, type of extraction vessel and shaker, and shaker speed. Differences in any one of these extraction parameters could lead to variation in levels of Cu, Fe, Mn, and Zn solubilized from soil. Standardization of extraction parameters as well as soil sample preparation is required to achieve quality control among soil testing laboratories.

Tedious concentration procedures are required for Cu determination by atomic absorption spectrophotometry if solutions contain <0.01 mg of Cu L⁻¹ (Mehlich & Bowling, 1975). This difficulty is not encountered for Fe, Mn, and Zn soil tests, except for procedures that solubilize only soil solu-

tion or exchangeable micronutrient cations. Similar amounts of Cu were extracted from organic and mineral-organic soils with 0.5 and 1.0 *M* HCl at soil/solution ratios of 1:2.5 and 1:5, respectively. Amounts of extractable Cu at these acid concentrations and soil/solution ratios were sufficiently high for Cu determination by atomic absorption spectrophotometry without Cu concentration. However, of amounts Cu extracted with lower HCl concentrations in the range of 0.075 to 0.2 *M* required Cu concentration prior to its determination by atomic absorption spectrophotometry.

Effects of H_3PO_4 concentration and extraction time on levels of extractable Mn were studied for two soils on which soybean had moderate to severe Mn deficiency (Hoff & Mederski, 1958). Extractable Mn increased with H_3PO_4 strengths from 0.003 to 0.333 *M* and with extraction times from 10 to 120 min. An acid concentration of 0.033 *M* and an extraction period of 60 min were selected because solubilization of unavailable Mn from Mn hydrous oxides would be less likely at this concentration than at higher concentrations and longer extraction times.

Salcedo and Warncke (1979) evaluated the effects of various soil/solution ratio and extraction time combinations on the amounts of Mn extracted with 0.1 *M* HCl, 0.033 *M* H_3PO_4 , DTPA-TEA, and 1.0 *M* NH_4OAc from 12 soils. Extraction periods of 10, 30, 60, and 120 min were combined with soil/solution ratios of 1:5, 1:10, 1:25 and, in addition, 1:2 for only the DTPA-TEA extractant. A soil/solution ratio of 1:25 with a shaking time of 120 min maximized extractable Mn by the four procedures. Correlations between Mn uptake by soybean plants grown in the greenhouse on the 12 soils and both DTPA-TEA and NH_4OAc extractable Mn were independent of the soil/solution ratio shaking-time combinations. Overall, the highest correlation with these combinations ($r = 0.92^{**}$, significant at $P = 0.01$) was obtained between Mn uptake by the soybean plants and Mn extracted by 0.033 *M* H_3PO_4 with a 1:5 soil/solution ratio and a 60-min shaking period.

The amount of Zn extracted by shaking 10 g of soil with 30 mL of 0.1 *M* HCl increased with shaking times from 1 to 240 min (Barrows & Drosdoff, 1960). A 2-min extraction period was chosen for the procedure because the amounts of Zn extracted from five soils did not differ greatly over the 1 to 60 min extraction periods. Sorensen et al. (1971) reported that the amounts of Fe, Mn, and Zn displaced by 0.1 *M* HCl from 18 soils increased with extraction times from 15 to 300 min and with increased soil-extraction solution ratios from 1:5 to 1:25. The magnitude of the increases varied widely among the soils for 0.1 *M* HCl extractable Zn, but varied little among the soils for extractable Fe and Mn.

During development of the DTPA-TEA soil test, it was found that extractable Cu, Fe, Mn, and Zn increased with extraction time (Lindsay & Norvell, 1978). The rate of release decreased sharply after the first hour for Cu, Fe, and Zn, and thus, a 2-h extraction time was selected for the procedure. Increases in temperature during the extraction from 15 to 35 °C increased amounts of the extractable cations and indicated the need for temperature control at 25 °C for the procedure. Higher DTPA concentrations increased the amount of extractable Cu, Fe, Mn, and Zn by placing greater stress on

the labile micronutrient forms. A DTPA concentration of 0.005 *M* was selected for the test because this concentration provided ample chelating capacity to remove measurable amounts of all four micronutrients and a sufficient excess to prevent competitive secondary interactions among the four metals.

Effects of type of extraction vessel and shaker, shaking speed and length, soil/solution ratio, and filtering time on amounts of DTPA-TEA extractable Cu, Fe, Mn, and Zn were evaluated for Colorado soils (Soltanpour et al., 1976). Extractable Cu, Fe, and Mn increased with soil/solution ratios from 1:2 to 1:6 for 10-g soil samples, whereas extractable Zn was not consistently increased with magnitude of the soil/solution ratios. At a shaker speed of 92 oscillations min^{-1} , amounts of extractable Cu, Fe, Mn, and Zn were higher when shaken in conical flasks than when shaken in rectilinear bottles. Increasing shaker speed increased the levels of metals extracted in rectilinear bottles more than in Erlenmeyer flasks. The difference was attributed to better mixing of soil and DTPA-TEA solution in the flasks. Higher amounts of Cu, Fe, Mn, and Zn were extracted when samples were shaken on a reciprocal shaker than on a rotary shaker. These data reflect the better mixing of soil and DTPA-TEA solution with the reciprocal shaker as compared with the settling of soil to the vessel bottom with use of the rotary shaker. Filtering time of up to 10 min had little effect on levels of extractable Cu, Fe, Mn, and Zn.

III. GREENHOUSE EVALUATION OF SOIL TESTS

Greenhouse evaluation of a soil test usually is undertaken once it is predicted through soil chemical principles that the extraction solution and conditions solubilize a proportionate part of the labile forms of a nutrient from different soils. The purpose of the greenhouse evaluation is to determine whether the soil test warrants field calibration. Field calibration is undertaken if the greenhouse evaluation indicates that the extractant and extraction conditions solubilize amounts of micronutrient cations that are closely related to plant-available forms in soils.

Simple and multiple correlation and regression analyses commonly are used for greenhouse research to evaluate whether the extraction solution and conditions solubilize the plant available forms of a nutrient from soil. One of the following dependent variables is selected for this evaluation: plant nutrient concentration in tissue, nutrient uptake, dry weight, or dry weight change in response to the nutrient application. The independent variable for these analyses usually is the amount of the nutrient solubilized from soil by the extraction solution and conditions. In some cases, independent variables such as soil pH, cation exchange capacity, clay content, and organic C concentrations have been included in the statistical analyses to account for a diversity of properties for soils included in the greenhouse evaluation.

Statistical data from greenhouse evaluation research require careful interpretation to determine whether the relationship is suitable for a soil test

to warrant field calibration. With a large number of observations, for example, a highly significant correlation ($\alpha = 0.01$) may be obtained with a relatively low r or R value. Due to this potential anomaly, a new procedure often is evaluated against a method that has been calibrated for similar soils. Frequently, the 0.1 M HCl extractable Zn (Wear & Sommer, 1948) or the DTPA-TEA extractable Cu, Fe, Mn, and Zn (Lindsay & Norvell, 1978) method has been included as a standard test in greenhouse evaluation studies.

Where growth responses are not obtained, correlation analyses may give invalid results because the relationship between the availability of a nutrient to plants and the amount of the extractable nutrient may not be linear in the deficiency range (Trierweiler & Lindsay, 1969). Consequently, there is little justification to extrapolate to the nutrient-deficiency range from regression equations developed with only soils that supply adequate amounts of the nutrient. It is, therefore, appropriate to use a group of soils that supply inadequate and adequate amounts of a nutrient to plants and to evaluate a new soil test procedure against yield response to application of a nutrient. This procedure necessitates control and micronutrient cation treatments to indicate whether soils supply insufficient or sufficient amounts of the micronutrients to plants in the greenhouse evaluation research.

The technique developed by Brown et al. (1962) is highly suitable for use in greenhouse evaluation studies to determine whether a new soil test warrants field calibration. They evaluated the suitability of dithizone- NH_4OAc (1.0 M NH_4OAc + 0.0004 M dithizone in CCl_4) extractable Zn as a procedure to detect soils with inadequate plant-available Zn. Zinc application increased dry weight of sweet corn on 27 of the 53 soils assayed in their greenhouse study. They presented data in bar graphs with levels of dithizone extractable Zn in ascending order from the origin along the abscissa and visually estimated the critical Zn level, which gave the best separation of soils into Zn deficient and sufficient categories, from the ordinate (Fig.

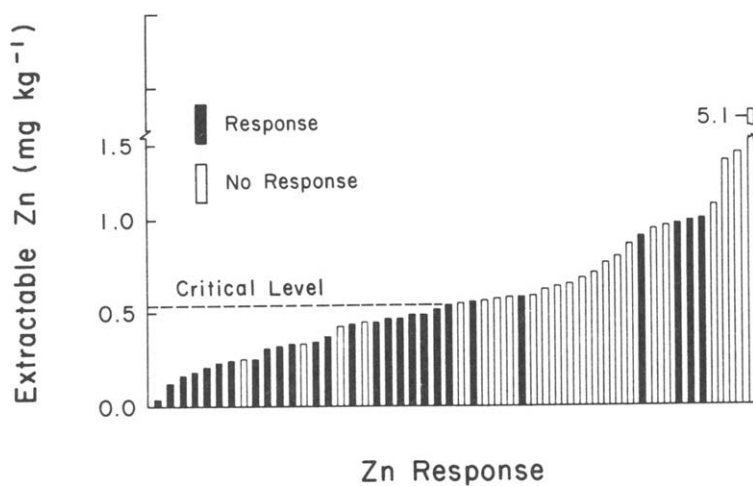


Fig. 9-1. Responses of sweet corn to soil-applied ZnSO_4 in relation to dithizone extractable Zn (Brown et al., 1962).

9-1). By this procedure, 84% of the soils below the critical level of 0.55 mg kg^{-1} supplied inadequate Zn, and 76% of the soils above this level supplied adequate Zn. An acceptable separation of nonresponsive and responsive soils may be obtained by this technique even where r values are not inordinately high between the extractable nutrient and tissue concentration or uptake of the nutrient from a series of soils (Trierweiler & Lindsay, 1969; Shuman et al., 1980).

The Cate-Nelson (Cate & Nelson, 1971) and linear plateau (Anderson & Nelson, 1975) models are highly suitable for use in greenhouse evaluation research. These models, like the graphic approach (Brown et al., 1962) indicate whether a soil test procedure warrants field calibration and provide a means to determine a critical nutrient level for a soil test. This critical level often is used for comparison purposes by others during completion of greenhouse evaluation research and frequently serves as a temporary critical level while a soil test is undergoing field calibration.

IV. FIELD CALIBRATION OF SOIL TESTS

The same statistical and graphic methods are used to obtain critical levels for a soil test in greenhouse evaluation and field calibration research. Critical levels for field calibration studies have been determined by use of the nutrient quantity extracted either alone or with other soil properties as the independent variable(s) in statistical analyses. The dependent variables used in these analyses have been the critical nutrient level in plant tissue or the yield response to micronutrient application. Critical levels for soil tests also have been obtained through comparison of amounts of an extractable nutrient with the presence or absence of deficiency symptoms. Reliance on plant physiology relationships dictates a need for knowledge in this area during completion of the field calibration research.

A. Differences in Plant Requirements

Caution must be exercised when the ability of soil to supply a micronutrient cation is evaluated by visual observation of deficiency symptoms. It is assumed by this technique that the micronutrient cation deficiency is recognizable, which as discussed below may not be valid for all micronutrient cation deficiencies. Increases in dry weight of soybean from Cu application occurred in greenhouse pots even though deficiency symptoms did not develop on plants (Makarim & Cox, 1983). The first visual symptom of Cu deficiency of field-grown wheat (*Triticum aestivum* L.) often is heads without a full complement of kernels and, when this symptom occurs, Cu application prior to the observation of symptoms increases seed yield (Alloway & Tills, 1984). Cotton (*Gossypium hirsutum* L.) seed yields were increased by Mn application in field experiments where Mn-deficiency symptoms were not observable on plants (Anderson & Boswell, 1968). A corn grain yield increase from Zn application occurred on a Norfolk loamy sand (fine-loamy, siliceous,

thermic Typic Paleudults) where plants on the control had mild Zn deficiency early in the growing season, but did not have symptoms late in the growing season (Schnappinger et al., 1969). It is apparent from these findings that reliance on visual observation of deficiency symptoms may lead to incorrect separation of soils into adequate and inadequate micronutrient cation availability groups.

Recognition that critical micronutrient cation concentrations vary with plant part and age and with cultivar is required where critical deficiency levels are used in soil test calibration research. Ohki et al. (1979) determined the critical Mn level for determinate soybean 'Ransom' based on blades from trifoliolate leaves at the R2 growth stage. The critical Mn levels in leaf blades sampled at position one (plant top) down the axis in sequential order to position five were 18, 13, 11, 11, and 10 mg of Mn kg⁻¹. Copper, Fe, Mn, and Zn concentrations from control and Mn treatments on three soils on which Mn application increased seed yields were as follows for uppermost matured trifoliolate leaves at the R1 growth stage: leaflet > entire leaf > petiole (Gettier et al., 1985a, b). Copper, Mn, and Zn concentrations were determined in the hypocotyl-crown, stem and leaves of first and second lateral branches, and the main stem above the branches from three peanut (*Arachis hypogaea* L.) cultivars at various growth stages (Martens et al., 1969). The main stem generally contained the highest Mn and Zn concentrations, whereas the hypocotyl-crown usually had the highest Cu concentrations. Differences among cultivars occurred in Mn and Zn concentrations of similar plant parts at one or more growth stages. All plant portions decreased in concentration of one or more micronutrient during the growing season, except the stemmy portion of the first and second lateral branches.

Translocation of micronutrient cations requires consideration where critical deficiency levels are used in soil test calibration research. Copper translocation in five tropical and five temperate pasture legumes was evaluated in greenhouse research by Andrew and Thorne (1962). More Cu accumulated in roots than in shoots of most species. The species that were most sensitive to Cu deficiency were less able to translocate Cu from root to shoots. Likewise, relatively little translocation of absorbed Cu occurred from roots to shoots in corn plants (Dragun et al., 1976) and citrus trees (Fiskell & Leonard, 1967). Proportionally more absorbed Mn and Zn are translocated from roots to shoots than either Cu or Fe (Logan & Chaney, 1983).

Low amounts of Cu translocation from roots to shoots may lead to low correlation between either plant Cu uptake or concentration and the Cu-supplying power of soil. The critical Cu level in plants is sufficiently low that small experimental errors may lead to low correlations where soils supply insufficient amounts of Cu. This relationship is further justification to calibrate micronutrient cation soil tests on the basis of yield response to Cu application rather than on the basis of critical Cu levels in plant tissue. An alternate calibration procedure is to relate the Cu concentration in roots to soil test values (Fiskell & Leonard, 1967). This procedure was feasible because the Cu concentrations in roots reflected rates of Cu application and because

the critical Cu level was higher in roots than in leaves. It is difficult, however, to obtain representative root samples.

Plants differ in sensitivities to Cu (Nelson et al., 1956; Andrew & Thorne, 1962; Reith, 1968), Fe (Olson & Carlson, 1950; Barak & Chen, 1982), Mn (Mascagni & Cox, 1984), and Zn (Massey, 1957; Brown et al., 1964) deficiencies under soil conditions conducive to these abnormalities. Copper deficiencies are common in cereal crops, Fe in peanut and sorghum, Mn in peanut and soybean, and Zn in corn and rice (*Oryza sativa* L.). Because plants vary widely in sensitivities to these micronutrient deficiencies, it is necessary to calibrate a soil test for each plant species or species with equal sensitivities.

B. Seasonal Effects on Plant Requirements

Climatic conditions affect yield response to micronutrient cation application. Surface application of Cu alleviated Cu deficiency of wheat in the greenhouse, but in-field trials on the same soils increases in vegetative growth from surface-applied Cu were not always accompanied by increases in grain yield (Grundon & Best, 1981). The difference between the greenhouse and the field research was attributed to variations in moisture content. Copper application did not increase yields in field experiments where negligible Cu was absorbed from the dry fertilizer zone. Infertile pollen, because of inadequate Cu absorption, led to failure of the wheat to produce grain.

Alloway and Tills (1984) pointed out that Cu deficiency occurs in crops when soil solution is unable to supply adequate Cu for plant uptake and that fast-growing crops require higher levels of soil solution Cu than do slow-growing crops. Therefore, increased availabilities of other nutrients, especially N, and highly productive crop cultivars will create a greater demand on the capacity of the solid phase to replenish Cu into soil solution. Since Cu is not readily translocated in plants, the deficiency develops during periods of rapid growth on soils with low solution Cu because of an insufficient rate of replenishment from the soil.

Excess irrigation water may cause Fe chlorosis in plants on calcareous soils (Lindsay & Thorne, 1954). In contrast, summer drought may cause death of seedlings that are susceptible to Fe chlorosis (Hutchinson, 1970). Iron relationships in soybean plants grown under different moisture regimes were studied by Elgala and Maier (1964). Plants were grown in the greenhouse on soils with 75 and 120% moisture-equivalent treatments. Higher moisture plants were chlorotic from Fe deficiency, and low moisture plants were normal. The lower amount of physiologically active Fe in chlorotic plants paralleled the higher amount of Ca and P in soil solution at the higher moisture content. Elgala and Maier (1964) concluded that the higher Ca and P uptake led to inactivation of Fe in cell walls and, thus, to less active Fe in protoplasm. It also is possible that the higher Ca activity led to more complexation of Ca in cell wall and membrane sites with a concomitant lower amount of transport of Fe into the protoplasm.

Manganese deficiencies commonly occur on poorly drained soils. Soil solution Mn activities in these soils often have a pronounced seasonal varia-

tion. Higher Mn activity in soil solution during periods of reducing conditions in winter and spring leads to higher Mn availability. As soils dry in the summer, the oxidizing conditions lead to decreases in soil solution Mn and thus to Mn deficiency. Soybean plants grown during the transition period may contain adequate Mn during early vegetative growth stages and, yet, develop the deficiency as late as 2 wk before flowering (Gettier et al., 1985c). For this reason, Mn concentrations in young plants are poorly related to the development of Mn deficiency later in the growing season.

Zinc-deficiency symptoms are generally most pronounced during a cool, wet spring and often disappear by mid-season (Bauer & Lindsay, 1965). The following explanations were presented for the relationship: (i) Zn uptake increases as the plant root system expands rapidly just prior to mid-season, and (ii) much of the available Zn comes from decomposition of organic residues for which the Zn release rate increases as greater biological activity occurs at the higher temperatures with advance of the growing season. In this research, incubation of soil at 43 °C for 1 to 3 wk increased Zn uptake by corn plants grown in the growth chamber and hence increased shoot and whole plant dry weight. Possible mechanisms proposed for the alteration of Zn availability by incubation at the higher temperature were release of natural chelating agents because of increased microbial growth or an increase in CO₂ pressure with an attendant increase in H₃O⁺ activity. Both factors increase the amounts of Zn in soil solution and thereby increase Zn availability.

V. SOIL TESTS FOR INDIVIDUAL MICRONUTRIENT CATION EXTRACTION

The current trend is to develop soil tests for simultaneous extraction and determination of micronutrient cations either alone or with macronutrients. This trend is desirable for rapid conveyance of soil test data to the crop producer at a reasonable cost. Through the years, reliable single micronutrient cation soil tests have been developed that currently are used in some soil-testing laboratories and which frequently are used as standard tests in greenhouse evaluation research.

A. Copper

Reith (1968) completed greenhouse research with 41 soils from north-east Scotland to evaluate the suitability of 0.05 M EDTA (pH 7.0) extractable Cu for detection of soils with inadequate available Cu. Although relatively low correlations were obtained between the EDTA extractable Cu with both grain yield ($r = 0.38^*$, significant at $P = 0.05$) and dry weight ($r = -0.54^{**}$) response of oat plants to Cu application under greenhouse conditions on the 41 soils, the test gave a good indication of grain yield response of oat and barley (*Hordeum vulgare* L.) plants to Cu application in field experiments on 30 soils. Grain yields were not restricted by Cu deficiency on soils with an EDTA extractable Cu concentration $> 1.1 \text{ mg kg}^{-1}$

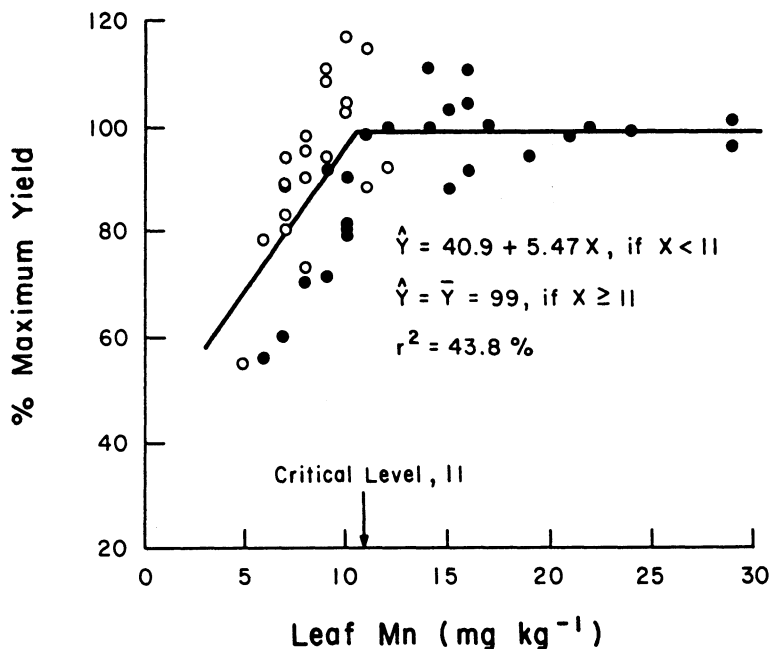


Fig. 9-2. The relationship between yield response and leaf Mn concentration in corn grown on two soils, which are represented by open and solid circles (Mascagni & Cox, 1984).

(Table 9-1). There were large increases in grain yields from Cu application on soils with $<0.75 \text{ mg kg}^{-1}$ of EDTA extractable Cu, and small increases on soils with EDTA-extractable Cu between 0.75 and 1.1 mg kg^{-1} .

In greenhouse research, the critical level of Cu extracted by the Mehlich-Bowling (0.5 M HCl , 0.016 M AlCl_3) method and growth response of corn, soybean, and wheat to Cu application was determined by the linear plateau model (Anderson & Nelson, 1975) to be 0.62 mg dm^{-3} of soil across the three crops (Makarim & Cox, 1983). The critical Cu level was extrapolated from the abscissa at the intersection of two straight lines, one in the linear portion and the other in the nonlinear portion, for a graph of percent maximum corn yield (ordinate) and extractable Cu (abscissa). Use of this technique is exemplified in Fig. 9-2 for research conducted by Mascagni and Cox (1984). Markarim and Cox (1983) obtained a critical level of 0.70 mg of Cu dm^{-3} of soil for the Mehlich-Bowling procedure by the Cate-Nelson model (Cate & Nelson, 1971) for soybean and wheat grown in 12 field experiments (Table 9-1). A Cate-Nelson plot is illustrated in Fig. 9-3 for research reported by Shuman et al. (1980).

B. Iron

Soil tests were developed for simultaneous extraction of Fe with other micronutrient cations either alone or with macronutrients (Soltanpour & Schwab, 1977; Lindsay & Norvell, 1978; Havlin & Soltanpour, 1981). Calibration data for these tests (Table 9-1) will be covered in a subsequent section.

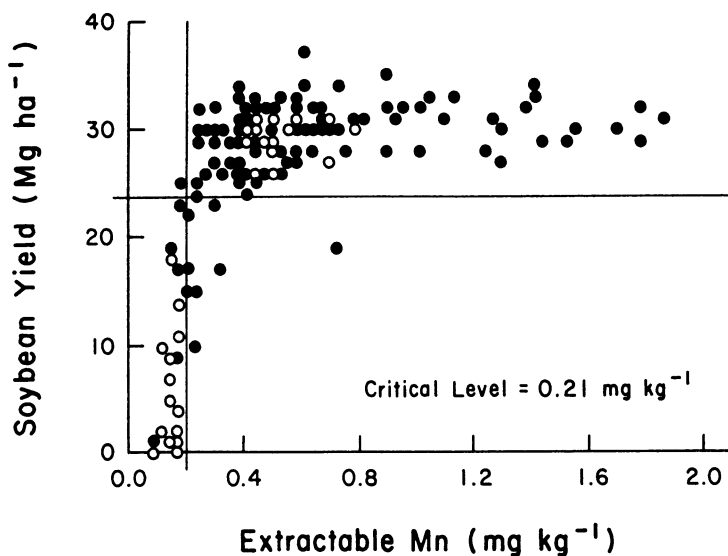


Fig. 9-3. Cate-Nelson plot for soybean seed yield vs. DTPA-TEA extractable Mn for two soils, which are represented by open and solid circles (Shuman et al., 1980).

C. Manganese

Eight soil tests were evaluated for their ability to predict uptake of native Mn by corn plants grown in the greenhouse on 63 Wisconsin soils (Browman et al., 1969). The soil tests evaluated were based on extraction with 1.0 *M* $\text{CH}_3\text{COONH}_4$ (pH 7.0); 0.5 *M* $\text{Mg}(\text{NO}_3)_2$; 0.2% hydroquinone in 1.0 *M* $\text{CH}_3\text{COONH}_4$ (pH 7.0); 0.033 *M* H_3PO_4 ; 3 *M* $\text{NH}_4\text{H}_2\text{PO}_4$; 1.5 *M* $\text{NH}_4\text{H}_2\text{PO}_4$; and EDTA- $(\text{NH}_4)_2\text{CO}_3$ [0.01 *M* EDTA, 1.0 *M* $(\text{NH}_4)_2\text{CO}_3$]. Of the soil tests, Mn uptake was most closely related to EDTA ($r = 0.60^{**}$) and H_3PO_4 ($r = 0.58^{**}$) extractable Mn. Regression equations were derived by comparing Mn uptake with each soil test in combination with pH and, from these analyses, the best prediction of Mn uptake was provided by 1.0 *M* $\text{CH}_3\text{COONH}_4$ extractable Mn and pH ($R = 0.73^{**}$). It was impossible to determine if the two variables would separate soils into Mn deficient and sufficient categories because a Mn treatment was not included in the greenhouse research.

Relationships between extractable Mn by nine procedures and levels of Mn in soybean tissue were evaluated for plants grown in 25 fields on Ohio soils (Hoff & Mederski, 1958). Soybean plants had Mn-deficiency symptoms on 18 of the 25 soils. Tissue Mn correlated most closely with 1.0 *M* $\text{NH}_4\text{H}_2\text{PO}_4$ ($r = 0.90^*$), alcoholic-hydroquinone ($r = 0.86^*$), and 0.033 *M* H_3PO_4 ($r = 0.86^*$) extractable Mn. Hoff and Mederski (1958) calibrated the three soil tests on the basis of presence or absence of Mn-deficiency symptoms of soybean plants at a specific Mn soil test level of (Table 9-1).

Hammes and Berger (1960b) assayed Mn availability to oat plants in the greenhouse on 20 different soils that had been stored in a moist condi-

tion prior to potting. Available soil Mn was estimated by extraction with 1.5 *M* $\text{NH}_4\text{H}_2\text{PO}_4$, 0.033 *M* H_3PO_4 , and 0.33 *M* H_3PO_4 on moist as well as air-dried samples. Correlations indicated that 0.033 *M* H_3PO_4 extractable Mn from moist samples gave the best relationship with Mn uptake by oat plants ($r = 0.85^{**}$). Since a Mn treatment was not used in the greenhouse research, it was not possible to determine if the H_3PO_4 extractable Mn procedure would separate soils into Mn deficient and sufficient categories.

In subsequent field research, Hammes and Berger (1960a) calibrated Mn soil tests with air-dry soil samples and oat grain yield response to Mn application in 25 field experiments. The soils used in this research were neutral to alkaline in reaction and developed from alkaline, lacustrine parent material. The 0.033 *M* H_3PO_4 and 1.5 *M* $\text{NH}_4\text{H}_2\text{PO}_4$ extractable Mn gave a much better separation of the 25 soils into Mn deficient and sufficient categories than did either 0.05 *M* EDTA or hydroquinone- NH_4OAc extractable Mn. Although they obtained suitable calibration data for all four procedures (Table 9-1), they recommended the H_3PO_4 soil test because of its high reliability and ease of usage. Based on the aforementioned greenhouse and field research and other greenhouse investigations (Randall et al., 1976; Salcedo & Warncke, 1979; Salcedo et al., 1979), the 0.033 *M* H_3PO_4 procedure currently is being used as a soil test for evaluation of the Mn status of soils for Mn-responsive crops in some North Central States (Whitney, 1980).

D. Zinc

Wear and Sommer (1948) provided the first calibration data for a micronutrient cation soil test. Their calibration data were based upon the occurrence of Zn-deficiency symptoms in corn grown in the field on 15 soils with pH levels from 4.7 to 6.2. Zinc-deficiency symptoms were not present in corn grown on seven soils with 0.1 *M* HCl extractable Zn levels $> 1.2 \text{ mg kg}^{-1}$ and were present on eight soils with extractable Zn levels in the range of 0.5 to 0.9 mg kg^{-1} . From these data, a critical level of 1.0 mg Zn kg^{-1} was selected for the 0.1 *M* HCl procedure (Table 9-1).

Subsequently, Wear and Evans (1968) compared the 0.1 *M* HCl and Mehlich-I (0.05 *M* HCl in 0.0125 *M* H_2SO_4) procedures as predictors of Zn uptake by corn and sorghum grown in the greenhouse on 12 sandy-textured soils with pH levels of 5.7 to 6.8. Correlation coefficients were higher for the Mehlich-I procedure and, therefore, they concluded that this procedure, which is routinely used in many southeastern laboratories, should replace the HCl extractable Zn soil test. The 0.1 *M* HCl, Mehlich-I, and DTPA-TEA procedures were calibrated for corn plants (Table 9-1) in a southeastern region project (Cox & Wear, 1977).

The 0.1 *M* HCl extractable Zn procedure extracts Zn from soil in excess of labile Zn. It dissolves portions of soil CaCO_3 and Al, Fe, and Mn hydrous oxides with a release of occluded Zn that, under normal soil conditions, is inaccessible for plant uptake (Trierweiler & Lindsay, 1969; Lauer, 1971). Nelson et al. (1959) developed a procedure to evaluate the Zn status of soils with two variables, 0.1 *M* HCl extractable Zn and titratable alka-

linity. The latter is the amount of acid required to acidify soil to pH 5.0. They obtained a good separation of soils with adequate or inadequate Zn for responsive crops even though the titratable alkalinity factor corrects all soils for release of the same concentrations of occluded Zn in acid-soluble components. Different amounts of occluded Zn in acid-soluble components among soils can lead to errors in the use of the technique. Shaw and Dean (1952) obtained a good separation of soils into Zn-deficient and nondeficient categories on the basis of the two variables, dithizone- NH_4OAc (pH 7.0) extractable Zn and soil pH. Their separation was based on the presence or absence of Zn-deficiency symptoms of crops grown on 41 soils from areas of Zn deficiency in the USA.

Trierweiler and Lindsay (1969) modified the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ procedure, which was originally developed by Viro (1955), to buffer at pH 8.6 with $(\text{NH}_4)_2\text{CO}_3$ and to contain 0.01 M EDTA. A good separation of 42 Colorado neutral and high lime soils into adequate and inadequate Zn categories for growth of corn in the greenhouse was obtained by the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ and dithizone- NH_4OAc procedures, but not by the 0.1 M HCl plus titratable alkalinity procedure. They used the approach of Brown et al. (1962) to obtain critical levels for the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ and dithizone- NH_4OAc procedures (Table 9-1), except that they divided soils into Zn deficient, Zn deficient with high P, and Zn-sufficient categories (Fig. 9-4). Justification for the modification was that it would be advisable to apply Zn if a soil was sufficiently near the deficient level and if the soil had a relatively high level of available P.

Precautions are necessary for use of the dithizone- NH_4OAc extractable Zn procedure because CCl_4 is hazardous to human health and, therefore, this procedure is less adaptable to routine use than is the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ procedure. The $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ method is superior to the acid extractant

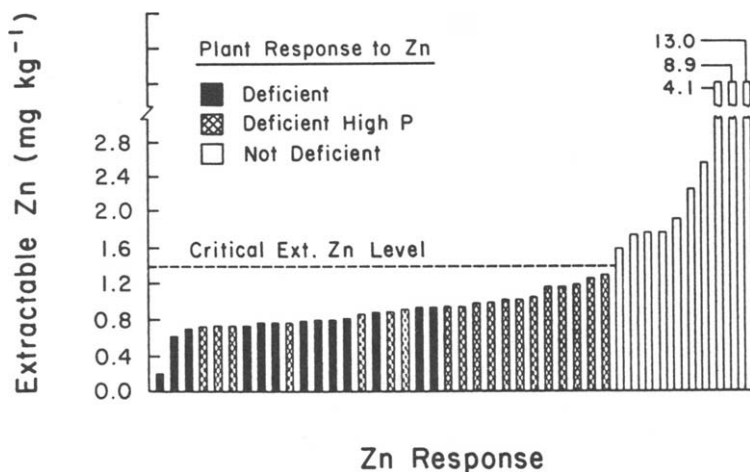


Fig. 9-4. The $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ extractable Zn of 42 Colorado soils in relation to Zn response of corn in the greenhouse (Trierweiler & Lindsay, 1969).

because, under conditions of high soil pH, this technique suppresses the carbonate and oxide dissolution and thereby avoids extraction of occluded Zn.

Alley et al. (1972) used the graphic approach developed by Brown et al. (1962) to calibrate the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ extractable Zn procedure with yield response of corn to Zn application. They estimated the critical level for $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$ extractable Zn to be 0.8 mg kg^{-1} for growth of corn under field conditions (Table 9-1). Zinc application increased corn grain yield on 5 of the 10 soils used in their calibration research.

The dithizone- NH_4OAc and DTPA-TEA extractable Zn procedures were about equally effective in separation of 92 California soils into Zn deficient and sufficient groups based on dry weight response of sweet corn to Zn application in the greenhouse (Brown et al., 1971). Both procedures were superior to the two-variable method, 0.1 M HCl and titratable alkalinity, for separating soils into Zn deficient and sufficient categories. An analysis of these data by a binomial statistical test indicated that the DTPA-TEA procedure was superior to the dithizone- NH_4OAc and 0.1 M HCl methods for separation of the 92 soils into Zn deficient and sufficient categories (Keisling & Mullinix, 1979). As use of the DTPA-TEA extraction procedure became prominent in the early 1970s, calibration research was discontinued for the $\text{EDTA}-(\text{NH}_4)_2\text{CO}_3$, dithizone- NH_4OAc , and 0.1 M HCl procedures, except for green gram (*Phaseolus aureus* Roxb.) and rice (Gupta & Mittal, 1981; Singh & Takkar, 1981).

VI. SOIL TESTS FOR MULTI-NUTRIENT EXTRACTION

Simultaneous extraction of micronutrient cations was initiated with the development of the DTPA-TEA procedure by Lindsay and Norvell (1969). Currently, this procedure is used in many soil-testing laboratories for detection of soils with inadequate amounts of Cu, Fe, Mn, and Zn for normal plant growth. The Mehlich-I (Nelson et al., 1953) and NH_4HCO_3 -DTPA (Soltanpour & Schwab, 1977) procedures presently are being used to detect soils that supply inadequate amounts of two or more micronutrient cations and certain macronutrients. It is expected that the Mehlich-III method (0.2 M HOAc , $0.25 \text{ M NH}_4\text{NO}_3$, $0.15 \text{ M NH}_4\text{F}$, 0.01 M HNO_3 , and 0.0005 M EDTA) will replace the Mehlich-I procedure in the future (Mehlich, 1984).

A. Simultaneous Extraction of Micronutrient Cations

The DTPA-TEA soil test was developed to identify near-neutral and calcareous soils with insufficient available Cu, Fe, Mn, or Zn for maximum crop yields (Lindsay & Norvell, 1978). The soil test successfully separated Colorado soils on the basis of crop response to Fe and Zn fertilization in greenhouse research. Critical Fe and Zn levels were based on visual observation of the soil test levels that separated responsive and nonresponsive soils (Table 9-1). Comparison of visual symptoms of Fe deficiency observed in the field with soil test results confirmed the applicability of the critical soil

test level for Fe. Since yield responses to Cu and Mn application were not obtained for the plants grown in the greenhouse, tentative critical DTPA-TEA extractable Cu and Mn levels were estimated to be 0.2 and 1.0 mg kg⁻¹, respectively (Lindsay & Norvell, 1978). The critical Mn level was based on the relationship between DTPA-TEA and hydroquinone-NH₄OAc extractable Mn and the calibration for the latter procedure. The critical Cu level was based on the DTPA-TEA extractable Cu concentration of 0.18 mg kg⁻¹ for two soils that supplied inadequate Cu to plants.

There is a need for a procedure to detect soils that supply inadequate amounts of both Cu and Zn for wetland rice because Cu deficiencies have been diagnosed on some soils and Zn deficiencies are widespread (Ponnamperuma et al., 1981). Relationships between Cu, Fe, Mn, and Zn concentrations in rice grown on flooded soils in the greenhouse and DTPA-TEA extractable Cu, Fe, Mn, and Zn in saturated 5-g soil samples incubated at 20°C for 21 d were investigated by Tiller et al. (1979). A correlation of $r = 0.79^{**}$ was obtained between Zn concentrations in young rice plants grown on 11 soils and levels of DTPA-TEA extractable Zn. Correlations for Cu, Fe, and Mn were nonsignificant.

Ponnamperuma et al. (1981) concluded that the DTPA-TEA procedure required too much labor, time, and cost and, therefore, determined whether a 0.05 M HCl extraction method would be as suitable as the DTPA-TEA procedure for detection of soils that supply inadequate Cu and Zn for rice production. Amounts of HCl extractable Zn correlated more closely with tissue Zn levels of rice grown in the greenhouse on 22 soils ($r = 0.88^{**}$) than did quantities of DTPA-TEA extractable Zn ($r = 0.31$ NS, nonsignificant at the 0.05 level). Likewise, the HCl extractable Cu correlated more closely with Cu concentration ($r = 0.74^{**}$) than did DTPA-TEA extractable Cu ($r = 0.20$ NS). A critical level of 1.0 mg of Zn kg⁻¹ was determined for the 0.05 M HCl extractable Zn procedure (Table 9-1) by the graphic method first used by Brown et al. (1962). A critical Zn level was not established for the DTPA-TEA procedure. It was not possible to estimate a critical Cu level for the HCl test because Cu application did not increase dry weight of rice plants grown in the greenhouse study. In another study, a correlation of $r = 0.98^{**}$ was obtained between Zn concentration in rice grown in the greenhouse and 0.05 M HCl extractable Zn in both dry and moist soil samples (Selvarajah et al., 1982). The pH of the nine soils used in this study ranged from 5.1 to 8.5.

B. Simultaneous Extraction of Micronutrient Cations and Macronutrients

The NH₄HCO₃-DTPA soil test was developed to simultaneously extract plant available P, K, Cu, Fe, Mn, NO₃-N, and Zn (Soltanpour & Schwab, 1977). Two criteria considered for the development of the test were as follows: (i) the soil test procedure should be rapid, reproducible, and economical, and (ii) the extraction of nutrients should be from the labile form that supplies those nutrients to plant roots (Havlin & Soltanpour, 1981). The ex-

tractant contains 1.0 M NH_4HCO_3 and 0.005 M DTPA adjusted to pH 7.6 (Soltanpour & Schwab, 1977). The high correlation between amounts of NH_4HCO_3 -DTPA and DTPA-TEA extractable Cu, Fe, Mn, and Zn ($r = 0.97\text{--}0.99^{**}$) coupled with evidence that the DTPA-TEA procedure extracts the labile micronutrient cations from soil (Lauer, 1971; Rule & Graham, 1976) suggests that the NH_4HCO_3 -DTPA procedure likewise would extract the labile forms of the micronutrients. Overall, the amount of Fe extracted by the two procedures was about the same, whereas the NH_4HCO_3 -DTPA method extracted 0.3, 0.8, and 0.5 mg kg^{-1} more Cu, Mn, and Zn, respectively. Critical levels for NH_4HCO_3 -DTPA extractable Cu, Fe, Mn, and Zn were established by regression procedures on the basis of DTPA-TEA extraction data for bean, corn, potato (*Solanum tuberosum* L.), sorghum, sudan [*Sorghum sudanense* (Piper) Stapf], and sorghum-sudan hybrids (Soltanpour & Schwab, 1977).

Improvements in computerized analytical instruments have provided stimulus for simultaneous multi-element determinations from a single solution. Soltanpour et al. (1979b) compared inductively coupled plasma optical emission spectrometry (ICP-OES) with atomic absorption spectrophotometry (AAS) for determination of Cu, Fe, K, Mn, and Zn in NH_4HCO_3 -DTPA extracts (Soltanpour & Schwab, 1977). They concluded that the ICP-OES and flame AAS analyses were comparable and, therefore, that ICP-OES, which has the advantage of simultaneous multi-element analysis, could be used for determination of Cu, Fe, K, Mn, and Zn in NH_4HCO_3 -DTPA extracts.

Greenhouse studies were carried out to evaluate the ability of the NH_4HCO_3 -DTPA extraction procedure to separate soils that supply adequate and inadequate amounts of Fe and Zn to plants (Havlin & Soltanpour, 1981). The NH_4HCO_3 -DTPA soil test was as effective as the DTPA-TEA soil test of Lindsay and Norvell (1978) in separating 40 soils into deficient and nondeficient categories. The critical Fe level for sorghum was 4.8 mg kg^{-1} for both tests, whereas the critical Zn levels for corn were 0.9 and 0.7 mg kg^{-1} for the NH_4HCO_3 -DTPA and DTPA-TEA procedure, respectively (Table 9-1). The NH_4HCO_3 -DTPA soil test is more economical than the DTPA-TEA procedure because the former simultaneously extracts both macronutrients and micronutrient cations. The advantages of the NH_4HCO_3 -DTPA procedure are as follows: (i) one extracting solution replaces NH_4OAc for K, NaHCO_3 for P, and DTPA; (ii) extraction time is rapid, i.e., 15 min; (iii) rapid analysis is possible with ICP-OES; (iv) results are very reproducible; and (v) there are savings in labor and reagents (Havlin & Soltanpour, 1981).

Baker (1973) developed a multi-nutrient soil test procedure based on theoretical ion exchange relationships between soil and equilibration solution that contains nutrients of interest, i.e., Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn. The equilibration solution has a lower DTPA concentration and is less buffered as compared to the DTPA-TEA extractant. This procedure has not been widely adapted for routine soil analysis possibly because of the overall complexity of the method.

Makarim and Cox (1983) calibrated the Mehlich-I (Nelson et al., 1953), Mehlich-Bowling (Mehlich & Bowling, 1975), NH_4HCO_3 -DTPA (Soltanpour & Schwab, 1977) and Mehlich-III (Mehlich, 1984) procedures for detection of soils with inadequate Cu levels. Organic and mineral soils located in the Atlantic Coastal Plain region were used in this greenhouse research. The percent maximum yield of corn, soybean, and wheat was related to the amounts of extractable Cu by the four procedures with a linear plateau model (Anderson & Nelson, 1975). The critical Cu levels in soil, which were estimated by the intersection of two straight lines in the model, were 0.26, 0.62, 0.53, and 0.37 mg dm^{-3} across crops, for the Mehlich-I, Mehlich-Bowling, NH_4HCO_3 -DTPA, and Mehlich-III procedures, respectively (Table 9-1).

The Mehlich-I procedure has been used for decades to predict the need for Ca, K, Mg, and P fertilization in southeastern USA. Cox (1968) refined the procedure to include soil pH with Mehlich-I extractable Mn as an indicator of Mn availability to soybean on 17 Atlantic Coastal Plain soils with pH levels from 5.2 to 7.1. He developed the following regression equation for the 17 field locations: $\Delta Y = 500 X_1 - 115 X_2 - 2405$; where ΔY = soybean yield response to Mn application in kg ha^{-1} , X_1 = soil pH, and X_2 = Mehlich-I extractable Mn in mg kg^{-1} . The equation accounted for 84% of the variation in soybean seed yield response to Mn application. He developed calibration data from the regression equation that accounted for the inverse relationship between soil pH and Mn availability (Table 9-1). He reasoned that a seed yield response of 67 kg ha^{-1} was required to cover Mn application costs and used this seed yield value to solve the regression equation to obtain the relationship with response probable and improbable at various levels of soil pH and extractable Mn.

Gettier et al. (1985c) modified the calibration for the Mehlich-I procedure on the basis of field research on 30 sites in the Atlantic Coastal Plain region. Manganese application increased soybean seed yields on 17 of the 30 sites. They obtained a prediction equation ($r = 0.68^{**}$) from these sites as follows: $Y = 205.71 - 24.71 X_1 + 7.03 X_2$; where Y = percent maximum yield response to Mn application on the 30 field sites, X_1 = soil pH, and X_2 = Mehlich-I extractable Mn in mg kg^{-1} . Their region of uncertain response to Mn application was obtained from solution of the regression equation for 80 to 100% of maximum yield. The critical level for the test was determined similarly with 90% of maximum yield (Table 9-1). The approaches by Gettier et al. (1985c) and Cox (1968) led to relatively similar results, except that the slope of the prediction equation was about 24% less for the equation by Cox (1968). Consequently, fewer incidences of Mn deficiency will be predicted by the calibration for the procedure reported by Gettier et al. (1985c) when the soil pH and Mehlich-I extractable Mn are >6.1 and 5.0 mg kg^{-1} , respectively, and more incidences of Mn deficiency will be predicted below these values.

Shuman et al. (1980) used the Cate and Nelson (1971) method for determination of the critical levels of soil tests to detect Mn deficiency of soybean on two soils. The method consists of construction of a graph with yield on the ordinate and extractable Mn on the abscissa. A cross is then placed

over data points and moved until the upper left and lower right quadrants have a minimum number of points (Fig. 9-3). The critical level is the amount of extractable Mn where the cross intersects the abscissa. Based on this method, the critical levels (Table 9-1) were 0.40 mg kg⁻¹ for NH₄HCO₃-DTPA, 0.22 mg kg⁻¹ for DTPA-TEA, 2.6 mg kg⁻¹ for Mehlich-I, and 1.8 mg kg⁻¹ for Mehlich-II (0.2 M NH₄Cl, 0.2 M HOAc, 0.015 M NH₄F, and 0.012 M HCl).

A second technique used by Shuman et al. (1980) to determine the Mn critical level for the soil tests was a regression approach based on the critical deficiency level of 12 mg of Mn kg⁻¹ in soybean leaves based on a 10% reduction in yield (Ohki et al., 1979). Linear regression equations were developed for the relationship of leaf Mn (*Y*) and extractable Mn (*X*). The critical Mn level for each soil test was then calculated by substitution of the critical tissue Mn concentration for the *Y* value in the linear portion of the regression equation. The respective critical levels for the NH₄HCO₃-DTPA and DTPA-TEA extractants of 0.33 and 0.24 mg of Mn kg⁻¹ were close to those determined by the Cate-Nelson method, whereas the critical values for the Mehlich-I and Mehlich-II extractants were much lower than those determined by the Cate-Nelson method. The Cate-Nelson approach was assumed by Shuman et al. (1980) to be more accurate than their regression technique, because the latter approach depends on the accuracy of the Mn critical level in tissue.

Quite often soil tests are evaluated on a weight basis by a researcher, whereas analyses are carried out with a volume of sample in soil testing laboratories. Therefore, Mascagni and Cox (1984, 1985) calibrated the Mehlich-I and Mehlich-III procedures on a volume basis for detection of Mn deficiency in soybean and corn (Table 9-1). Their calibration research was based on one location in the Atlantic Coastal Plain region for corn and on 38 experiment years in this region for soybean. The importance of this research is indicated by the fact that future usage of the Mehlich-III procedure for estimation of available Ca, K, Mg, Mn, and Zn is anticipated in southeastern USA.

VII. ADDITIONAL SOIL TEST USES

The micronutrient cation soil tests were developed to identify agricultural soils with inadequate available Cu, Fe, Mn, or Zn for high crop yields. Because the soil tests extract labile forms of the micronutrients, they have additional applications. The soil tests have been used rather extensively in research on downward movement and reversion of micronutrients in soils. Frequently, soil tests are used to evaluate these reactions in soils that received high rates of waste products such as municipal sludge and high Cu manure (Payne et al., 1988; Rappaport et al., 1988).

A. Downward Movement

Less variation in micronutrient cation concentrations often occurs in labile cation forms determined with soil tests than in total concentrations

from the same soil. This difference probably reflects less heterogeneity of an element in the labile form than in the nonlabile form in soil. For this reason, soil tests have been used to monitor downward movement of the micronutrient cations under laboratory and field conditions.

Wilson et al. (1981) investigated the amount of leaching from three annual applications of 56 kg of Mn ha⁻¹ in an Olustee-Leefield sand (sandy, siliceous, thermic Ultic Haplaquod-loamy, siliceous, thermic Arenic Plint-aquic Paleudult) with soil pH values of 6.2 to 6.7. Data from samples obtained at different depths showed that most of the DTPA-TEA and Mehlich-I extractable Mn remained in the upper 30 cm, i.e., in the soybean root zone. These data indicated that low Mn uptake by soybean was not due to leaching of Mn, but rather to formation of insoluble Mn hydrous oxides in this soil.

The Zn distribution in Nebraska sandhill soils where cropping changed from native grass to intensive irrigated corn was studied over a 5-yr period (Rehm et al., 1984). Zinc extracted with 0.1 M HCl indicated negligible downward movement of Zn from five annual applications of 13.6 kg of Zn ha⁻¹ in a Thurman loamy fine sand (sandy, mixed, mesic Udorthentic Haplustoll). It was concluded that there was little, if any, potential for movement of Zn into the groundwater even though relatively high rates had repeatedly been used on the irrigated sandy soil.

B. Reversion Reactions

There is a tendency for micronutrient cations applied to soils to revert from labile forms to less soluble nonlabile forms with time. Reversion rates of the micronutrient cations to plant-unavailable forms have been evaluated with soil tests. Reversion of broadcast Zn mixed into the surface 20 cm of Ritzville fine sandy loam (coarse-silty, mixed, mesic Calciorthidic Haploxeroll) was studied annually for 6 yr after Zn application (Boawn et al., 1960). There was a decrease in 0.1 M HCl extractable Zn over the 6-yr period where 2.2, 4.4, 8.8, and 27.6 kg of Zn ha⁻¹ as ZnSO₄ had been applied to the soil. After 6 yr, the extractable Zn levels were higher where Zn was applied than in the control treatment and the increases in extractable Zn over the control treatment increased with rate of Zn application. These data showed that applied Zn had a residual effect over several years. Much of the Zn applied as ZnSO₄ at rates of 112 and 336 kg of Zn ha⁻¹ remained in a dithizone-NH₄OAc extractable form after 3 and 4 yr in a Tulare clay loam (fine montmorillonitic (calcareous), thermic Vertic Haplaquoll) and a peaty muck, respectively (Brown et al. 1962).

Eleven soils were fertilized with Cu, Fe, Mn, and Zn and examined periodically during a 14-wk incubation period for concentrations of the DTPA-TEA extractable micronutrients (Follett & Lindsay, 1971). During the incubation period, DTPA-TEA extractable nutrients declined to 61% of the original value for Cu, 14% for Mn, and 44% for Zn where these metals were supplied as sulfates. Only 20% of the Fe added as FeSO₄·7H₂O remained extractable at 1 wk, whereas 70% of the Fe added as FeEDDHA was extractable at 7 wk and 26% at 14 wk. These results are in general agreement with

reported residual response from these fertilizers and suggest that the DTPA-TEA soil test may be used to monitor the availability of micronutrient cations in fertilized as well as unfertilized soils. A similar conclusion can be made for NH_4HCO_3 -DTPA extractable Fe and Zn based on experimental data from greenhouse research by Havlin and Soltanpour (1984).

Mehlich-I extractable Mn in a Dragston fine sandy loam (coarse-loamy, mixed, thermic Aeric Ochraquult) 1 yr after application of 0, 10, 20, 40, and 50 kg of Mn ha^{-1} as MnSO_4 correlated closely with rate of Mn application ($r = 0.99^{**}$) and with soybean seed yields ($r = 0.96^{**}$) (Gettier et al., 1984). Although these data show that there was a residual effect of Mn the second year after application, yields were higher from re-application of Mn even where as much as 60 kg of Mn ha^{-1} had originally been applied to the soil. These data are in general agreement with the finding that Mn fertilizers remain available in highly acid soils but rapidly oxidize and precipitate to less-available forms under near-neutral and alkaline conditions. The data illustrate that good correlations can be obtained between soil test data and crop yields from micronutrient cation application on one soil or a group of soils with similar properties. Often, however, unsuitable relationships are obtained when a soil test is used to predict micronutrient cation availabilities from a group of soils with diverse properties.

VIII. LIMITATIONS OF SOIL TESTS

A. Soil Variability and Sampling

The distribution of micronutrient cation deficiencies often varies widely in fields. These deficiencies frequently occur in areas of <1 ha scattered throughout a field or in extensive areas with mild to severe or almost uniform deficiencies. Variable patterns of these deficiencies sometimes reflect natural heterogeneity in chemical and physical properties of different soils from drainage, P availability, pH, lime content, and other factors. In some cases, the different deficiency patterns within a field are related to variable pH changes from limestone application in soils with different buffer capacities or to variable P availabilities from P application in soils with different phosphate equilibria. Commonly, the micronutrient deficiencies reflect non-uniformity in limestone or P application.

Soil micro-heterogeneity could lead to incorrect interpretation of soil test data. This incorrect interpretation could occur for soils where soil acidity was incompletely neutralized by limestone application because of a short-term equilibration period. In this case, the applied limestone could neutralize an acidic extraction solution and, yet, have little effect on plant uptake of the micronutrient cations.

The first decision in obtaining a sample for evaluation of the micronutrient cation status from a field with much soil variation is whether to obtain a composite sample of each soil type or to obtain a composite sample from the entire field. One composite sample may mask the actual occurrence

of the deficiencies. There is not one prescribed methodology for selection of either multiple or single composite samples from a field. Instead, the need for single or multiple composite samples from a field is based on a case-by-case consideration of the importance of a representative sample for a specific area.

B. Soils with Diverse Properties

The DTPA-TEA soil test was developed to detect Cu, Fe, Mn, and Zn deficiencies in alkaline and calcareous soils. Application of this procedure to noncalcareous soils may require inclusion of soil pH along with amounts of DTPA-TEA extractable micronutrient cations in models for prediction of these micronutrient deficiencies. For example, the need for Zn fertilization in corn production on Ontario soils is predicted from the following model (Bates, 1984): $\text{Zn-availability index} = 203 + 4.5(\text{DTPA extractable Zn}) - 50.7(\text{soil pH}) + 3.33(\text{soil pH})^2$. This equation adjusts the Zn-availability index for soil pH up to approximately 7.0 and provides little adjustment for pH values between 7.0 and 8.0. A Zn-availability index below 15 indicates potential Zn deficiency in corn.

Logically, extractable P, soil pH, and extractable Cu, Fe, or Zn could be included in models for prediction of the micronutrient availabilities, because, at a given level of extractable Cu, Fe, and Zn, these micronutrient availabilities decrease with an increase in both available P and soil pH. A good relationship ($r = 0.945^{**}$) was shown between actual Zn uptake and Zn uptake predicted by the following equation in corn plants grown under greenhouse conditions:

$$Y = 780.2 + 68.8X_1 - 101.3X_2 - 0.4X_3$$

where Y = Zn uptake by corn plants, X_1 = Mehlich-I extractable Zn, X_2 = soil pH, and X_3 = Mehlich-I extractable P (Alley et al., 1972). This equation accurately separated 9 of 10 soils into Zn deficient and sufficient categories. The appeal of this approach is that each of these soil parameters is routinely determined in soil testing laboratories and, hence, recommendations can be computerized with ease.

C. Seasonal Weather Fluctuations

The micronutrient soil test results indicate only whether a micronutrient cation deficiency is likely to occur. The test results do not indicate the actual magnitude in yield increase from application of the micronutrient. An actual yield increase is weather dependent, i.e., a greater yield increase from micronutrient application occurs during a growing season with weather conditions conducive to high yields. In fact, statistical procedures often are not sufficiently sensitive to indicate a micronutrient cation deficiency when small yield increases are obtained because of a drought in non-irrigated crops. This lack of sensitivity leads to an error in soil test calibration, for no response

may be obtained on a soil when yields are low, whereas a yield response would have been obtained on the soil under environmental conditions conducive to high yields.

Manganese deficiency of field crops is very weather dependent. Often this deficiency occurs when an inadequate amount of Mn is supplied to plants after Mn is oxidized and forms insoluble hydrous oxides. In some cases, Mn soil test data are used to flag areas of potential Mn deficiency, and foliar Mn is applied to plants when Mn-deficiency symptoms are observable. This method is suitable for correction of Mn deficiency in soybean because the plant has characteristic Mn-deficiency symptoms and relatively high yields can be obtained by correction of Mn deficiency by foliar Mn application (Gettier et al., 1985a). The method is unsuitable, however, in cases of incipient micronutrient deficiencies.

D. Recommendations from Soil Test Results

A major problem with micronutrient cation recommendations is the zone of uncertainty about a soil test critical level where a micronutrient deficiency may or may not occur. In these cases, it is necessary to consider economic factors in development of a recommendation for micronutrient application. The cost/benefit ratio must be considered for various crop and management regimes for these recommendations. The main danger is that individuals responsible for the recommendations may lack the background to recognize the existence of the zone of uncertainty for soil test data and, therefore, will not consider economic factors along with soil test data for fertilizer recommendations.

IX. COMMENTARY

The goal in development of a micronutrient cation soil test is to extract a proportionate part of the labile forms from different soils. This goal can be achieved with present knowledge of soil chemistry as is shown by, for example, the good separation of soils into Cu, Fe, Mn, and Zn deficient and sufficient categories by the DTPA-TEA procedure. Development of the many satisfactory soil tests is an accomplishment of considerable magnitude when one considers the labile micronutrients are extracted from a dry or moist sample under laboratory conditions, and amounts of labile micronutrients vary under diverse environmental conditions while plants are grown on the field sample site.

Although satisfaction can be taken in past achievements, it is recognized that improvements in micronutrient cation soil testing are needed in the future. Improved tests must be developed as advances are attained in soil micronutrient chemistry and plant physiology. More field calibration data are needed for present tests to improve fertilizer recommendations for Cu, Fe, Mn, and Zn. It would be appropriate to direct more attention to standardization of extraction conditions among laboratories to provide the quality

control necessary for valid interpretation of the data. More emphasis should be placed on procedures for simultaneous extraction of both macronutrients and micronutrients by the same soil test procedure to provide more rapid transference of fertilizer recommendations to the crop producer at a lower cost and to facilitate the consideration of ion uptake interactions. The accuracy for prediction of a specific nutrient must not be compromised in the development of multi-nutrient soil tests.

It is recognized that a soil test for a micronutrient cation is just one component that can be applied to an overall systems approach to predict whether a Cu, Fe, Mn, or Zn deficiency of a plant will occur on a specific soil. Other logical components of this system would be the plant grown, variable plant response to different weather conditions such as temperature and moisture, and differences in properties from soil to soil that affect crop uptake of the elements. In the future, more attention should be directed toward an overall systems approach rather than to the sole use of a micronutrient cation soil test for prediction of fertilizer needs.

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Chapter 10

Testing Soils for Sulfur, Boron, Molybdenum, and Chlorine¹

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The nutrient elements S, B, Mo, and Cl are all relatively mobile in soils. This, in general, is due to their existence as relatively large anions (Cl^-) or oxo anions (SO_4^{2-} and MoO_4^{2-}) that form relatively soluble compounds with the common cations abundant in soils, or as in the case of B, chemical stability as a soluble uncharged molecule (H_3BO_3). Plants absorb the nutrients primarily in these chemical forms. The commonly formed alkali metal and alkaline earth compounds of the elements, when present in solid phase, are sufficiently soluble to provide a more than adequate supply of the nutrients for crops.

Except for S, the elements are required in such small amounts by plants that they are commonly categorized as micronutrients. For this reason, crop deficiencies are the exception rather than the rule, even in humid environments where the potential for leaching is high. For different reasons, S deficiencies are also somewhat uncommon and the economic impact of shortages of these elements in crop production is small relative to N, P, and K. Consequently, the evolution of soil testing which has led to reliable procedures used in routine testing for N, P, and K has not occurred to the same degree for S, B, Mo, and Cl. In those environments and cropping systems where these elements are lacking, correctly identifying the deficiency and degree to which it exists has great economic importance and may be aided through soil testing as described in the following sections. These sections will consider in order each element with respect to (i) extraction procedures, (ii) analytical procedures, and (iii) interpretation.

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I. SULFUR

A. Extraction Procedures

Successful procedures for estimating available S in soils have centered on extraction of $\text{SO}_4\text{-S}$ using dilute acids or dilute salt solutions. The principle involved is to remove water soluble, easily exchangeable, and adsorbed or labile S. Attempts to measure mineralizable S have met the same obstacles as for mineralizable N and hence mineralizable S has not been a component of successful S soil tests. At least 20 different reagents or reagent concentrations have been successful to some degree for extracting available S from soils (Table 10-1). It is obvious that many solutions, including water, have potential for extracting available S from soils. Several factors account for the apparent success or failure of extraction procedures for estimating available S.

In arid and semiarid regions of the world, where leaching has been minimal and soils contain an abundance of simple sulfate salts, procedures which extract water soluble sulfate can easily differentiate nonresponsive soils from soils that may potentially respond to added S. In more humid regions of the world, exchangeable and loosely bound or labile forms of S become increasingly more important sources of S to sustain crop production. Extracting solutions that contain a replacing ion such as phosphate are likely to be more successful in these climates.

Weak electrolyte solutions of a monovalent cation often extract considerable organic matter that may seriously interfere with sulfate analysis.

Table 10-1. Reagents for extracting available S.

Reagent	Reference
H_2O	Bansal et al., 1979
HCl (0.001 <i>M</i>)	Bansal et al., 1979
HCl (0.05 <i>M</i>)	Islam & Ponnampereuma, 1982
LiCl (0.1 <i>M</i>)	Islam & Ponnampereuma, 1982
LiCl (0.01 <i>M</i>)	Maynard et al., 1987
NaCl (10 g L^{-1})	Bansal et al., 1979
KCl (0.01 <i>M</i>)	Maynard et al., 1987
CaCl_2 (0.01 <i>M</i>)	Yli-Halla, 1987
CaCl_2 (1.5 g L^{-1})	Palaskar & Ghosh, 1985
NH_4OAc (1.0 <i>M</i>)	Palaskar & Ghosh, 1985
NH_4OAc (0.5 <i>M</i>)	Islam & Ponnampereuma, 1982
NH_4OAc (0.003 <i>M</i>)	Maynard et al., 1987
NH_4Cl (0.003 <i>M</i>)	Maynard et al., 1987
NH_4Cl (0.01 <i>M</i>)	Maynard et al., 1987
$\text{Mg}(\text{OAc})_2$ (1.0 <i>M</i> , pH 7.0)	Palaskar & GHosh, 1985
NaHCO_3 (0.5 <i>M</i> NaHCO_3)	Tiwari et al., 1983
NaOAc (1.0 <i>M</i>) + HOAc (to pH 4.8)	Bansal & Pal, 1987
NH_4OAc (0.5 <i>M</i>) + HOAc (0.5 <i>M</i>)	Yli-Halla, 1987
KH_2PO_4 (500 mg L^{-1} P)	Bansal et al., 1983
$\text{Ca}(\text{H}_2\text{PO}_4)_2$ (500 mg L^{-1} P)	Islam & Bhuiyan, 1988
$\text{Ca}(\text{H}_2\text{PO}_4)_2$ (500 mg L^{-1} P + 2 <i>M</i> HOAc)	Hoef et al., 1973

This is especially true when turbidimetric analysis with Ba is used. For these extractants, decolorization using charcoal must precede the final analysis. Extractants using Ca or Mg salts will usually provide clear, colorless solutions for analysis. Stepwise procedures for extraction of soluble and soluble plus adsorbed S are detailed elsewhere (Tabatabai, 1982).

B. Analytical Procedures

There are several analytical techniques available for measuring extracted soil S. The most common method in the USA is the turbidimetric analysis after reaction of sulfate with Ba (Johnson, 1987). The foundation of this method is the low solubility of solid BaSO_4 that forms under controlled conditions when fine BaCl_2 crystals are added to the extract containing sulfate. This method is accurate for mg kg^{-1} levels and, while somewhat cumbersome, usually can be performed with existing equipment (Eik, 1980). Modifications of the turbidimetric method include analysis of the precipitated Ba by atomic absorption analysis (Oeien, 1979) and the use of autoanalyzers to help standardize conditions and speed analysis to as many as 200 samples/d (Wall et al., 1980; Lea & Wells, 1980).

More recent work has demonstrated successful analysis of S in soil extracts by ion chromatography and inductively coupled plasma (ICP) atomic emission spectrometry (Maynard et al., 1987). Analysis by ICP has been shown to give higher results (Yli-Halla, 1987) than turbidimetric analysis and may include S forms other than sulfate in the extract.

The colorimetric procedures, using sulfate reduction and subsequent reaction with methylene blue (Johnson & Nishita, 1952), continues to be used and improved to provide more rapid and inexpensive analysis (Kowalenko, 1985; Pirela & Tabatabai, 1987).

These procedures all have merit and should be considered when they take advantage of existing equipment and advanced technology to allow rapid accurate analysis.

C. Interpretation

Sulfur soil test interpretations have taken many forms, and include relating critical soil concentration to crop response parameters such as yield, plant S concentration, or N/S ratio. Although crop yield is usually the most important index for assessing adequate nutrition, many studies have depended upon plant response in the greenhouse for evaluating S soil tests. In these studies, plant S concentration and N/S ratios have often been used.

Attempts to calibrate S soil tests have been unsuccessful for many of the same reasons N soil test calibrations have failed. Principle reasons among these is the fact that the primary nutrient form absorbed, sulfate like nitrate is relatively mobile in the soil. Hence, interpretation of the soil test must take into account the production level or yield goal (see chapter 6 in this book, by Dahnke and Johnson). Consequently, greenhouse studies have limited value for identifying a critical soil test level because the S-supplying soil

volume is dependent on pot or container size that is usually restrictive relative to field conditions.

Unlike N fertilizer needs, S deficiencies are seldom more than a few kg/ha (or lb/acre) and may be corrected by applying about 1/20 of the N requirement for the crop. For this reason, instead of trying to determine accurately an existing small deficiency of S by use of a soil test, an adequate amount of S (10–15 kg/ha) is often recommended for crops growing in deep, sandy soils, susceptible to S deficiency (Johnson, 1987).

Critical extractable $\text{SO}_4\text{-S}$ levels vary greatly depending upon the extractant used and whether or not the investigation was performed in the field or greenhouse; choice of crop has minor influence. A critical level of 30 mg/kg of S, extracted by NH_4OAc , has been reported for corn (*Zea mays* L.) (Palaskar & Ghosh, 1985), rice (*Oryza sativa* L.) (Islam & Ponnampereuma, 1982), and cabbage (*Brassica oleracea* L.) (Palaskar & Ghosh, 1981). By comparison, a critical level of about 10 mg/kg has commonly been reported for phosphate-containing extractants (Bansal et al., 1979; Islam & Ponnampereuma, 1982; Bansal et al., 1983; Palaskar & Ghosh, 1985; Islam & Bhuiyan, 1988). Available S in subsoil should also be measured to accurately determine crop needs. When subsoil S has been included critical levels as low as 3.5 mg/kg have been identified using phosphate solutions for extraction (White et al., 1981).

Using S soil tests, which in themselves are difficult to interpret, as a means of predicting response to S fertilizer often fails because of extraneous or incidental S additions to the field. Amounts of S ranging from 10 to 30 kg/ha may be supplied from rainfall annually (Sharpley et al., 1985). Similar levels of S may be supplied from soil organic matter mineralization, manures, other fertilizers, soil amendments, pesticides, atmospheric SO_2 or particulate deposition.

II. BORON

A. Extraction Procedures

The most widely used and investigated B soil test is the hot water extraction method (Berger & Truog, 1939). Other successful methods including variations on the hot water extraction, are extractions with Morgan's reagent (NaOAc-HOAc) (Lombin, 1985), mannitol (Jin et al., 1988), CaCl_2 + mannitol (Cartwright et al., 1983), and hot CaCl_2 (Parker & Gardner, 1981; Aitken et al., 1987; Jeffrey & McCallum, 1988).

The hot water extraction method has consistently proven to be a reliable method for estimating available B. The major drawback to this method is that it requires refluxing the boiling soil-water mixture. This requirement has made it difficult to adapt the method to rapid routine analysis for many samples. Refluxing the boiling sample in weak CaCl_2 solutions (0.01–0.02 M) usually provides a clear, colorless extract without altering the amount of B extracted. This is a significant improvement when colorimetric analysis

is used because it eliminates the need to add charcoal as a decolorizing agent. In addition to saving a step, it also removes a source of negative error in the extraction (Gupta, 1979; Parker & Gardner, 1981).

Additional improvements in the hot water extraction in recent time have been the consideration of lengthening the extraction period and substitution of plastic containers for glass-refluxing equipment. Extending the boiling time from 5 to 10 min gives more consistent results (Odom, 1980) without complicating the procedure. Boiling the soil-water mixture in plastic pouches, instead of refluxing with glass, offers a major advancement in the method with the advantage of lower equipment cost, less labor, and improved sample turn-around time (Mahler et al., 1984). Similar advantages have been obtained by performing the extraction in plastic tubes heated in an aluminum block (Nilsson, 1986).

B. Analytical Procedures

Colorimetric analysis using either curcumin or azomethine-H have been the most common methods of measuring extracted soil B. Continued improvements in these methods have resulted in eliminating interferences, improving sensitivity, and adaptation to automated analysis (Wikner & Upstroem, 1980; Parker & Gardner, 1981; Porter et al., 1981). A standard procedure for these methods of analysis and the preceding soil extraction are given in detail elsewhere (Bingham, 1982).

Recent technological advances in analysis of elements by emission spectrometry have resulted in this becoming an attractive analytical tool for soil testing. Both ICP and direct current plasma (DCP) have been found acceptable alternatives to the colorimetric procedures (Gestering & Soltanpour, 1981; Nilsson & Jennische, 1986; Jeffrey & McCallum, 1988). Using either ICP or DCP instruments, the analysis is fast because soil extracts may be analyzed directly. Emission analysis is relatively free of interferences and provides excellent detection limits and precision.

C. Interpretation

Boron nutrient requirements are dependent on the crop to be grown and its anticipated yield. Requirements for most crops, however, are usually met when soils contain only 0.5 to 1.0 mg kg⁻¹ of hot water soluble B, and levels above about 5 mg kg⁻¹ are likely to be toxic (Ponnamperuma et al., 1981). For this reason, deficiencies are easily corrected by adding small amounts (0.5–1.0 kg/ha) of B and care must be taken to avoid adding too much and causing a toxic condition.

III. MOLYBDENUM

Molybdenum availability in soils has not been extensively researched, in large part because deficiencies are scarce. Secondly when deficiencies have been suspected, factors other than soil test availability indexes have shown

to be just as useful for predicting response to Mo additions. While this latter conditional application of the soil test result is not unusual among micro-nutrient soil tests, having to measure other soil parameters does sometimes detract from soil test application.

A. Extraction Procedure

The most commonly used extractant has been ammonium oxalate (Grigg, 1953). However, even this extractant has not been consistently successful and, in spite of early promise, it has not been better for diagnosing Mo deficiency than soil type (Grigg, 1960). In more recent work (Lombin, 1985), the Mo extracted by ammonium oxalate was only poorly related ($R^2 = 0.64$) to Mo uptake by peanut (*Arachis hypogaea* L.) in the greenhouse when soil organic matter was included as an independent variable. An intensive study involving several soils and crops in a large geographical area of the southeastern USA found acid oxalate extractable Mo poorly related to plant parameters associated with available soil Mo (Mortvedt & Anderson, 1982). Correlations of soil Mo and plant Mo were not statistically significant for forage legumes. Relative forage yield and plant Mo concentration were highly correlated to soil pH, however. The correlation with these crop parameters was only slightly improved by including both soil pH and soil Mo. Resulting R^2 values were only about 0.5 indicating poor predictive ability of the soil tests. Although the acid ammonium oxalate procedure has not been a successful extractant from the standpoint of identifying Mo-deficiency conditions, it still appears to hold the most promise for measuring available Mo.

B. Analytical Procedures

Analytical methods must be sensitive to measure extracted Mo since the concentrations will usually be in the range of about 10 to 50 $\mu\text{g/L}$. Successful methods include graphite furnace-atomic absorption spectrometry (Mortvedt & Anderson, 1982) and direct-current plasma emission spectrometry (Pierzynski et al., 1986).

C. Interpretation

Critical levels of extractable available Mo remain unknown for lack of suitable extracting reagents or Mo-deficient soils. Identifying critical levels is made more difficult by the fact that plant response in marginally deficient soils appears to be influenced more by liming than application of Mo (Mortvedt & Anderson, 1982).

IV. CHLORINE

Chlorine has been recognized as an essential plant nutrient for many years. However, because the element is so commonly present in the environ-

ment, deficiencies in the field are rare, if not absent altogether. Interpretation of field responses to chloride fertilizers are confounded by the prophylactic properties of the element (Christensen et al., 1981). Nevertheless, recent work presents strong evidence for chloride insufficiencies in the Northern Great Plains of the USA (Fixen et al., 1986b). Low rainfall and little or no need for K fertilizer (KCl) are somewhat unique features of this large landlocked geographical area.

A. Extraction Procedures

Chloride can be extracted from soils using water (Fixen et al., 1988) or any weak electrolyte since the common Cl salts are highly water soluble. Choice of extractant may be influenced by analytical method and compatibility with simultaneous extraction of other elements. Care must be taken to avoid contamination from dust, water, glassware, filter paper, paper bags, perspiration, and many common cleaning agents (Fixen et al., 1988).

B. Analytical Procedures

Several methods of analysis are available for quantifying extractable Cl. Procedures for colorimetric analysis using mercury (II) thiocyanate; potentiometric analysis using a Cl^- electrode; and analysis by ion chromatography have been described in detail (Fixen et al., 1988). Titration of Cl in the soil extract using AgNO_3 has also been used successfully (Fixen et al., 1986a).

C. Interpretation

The critical level of extractable Cl is still poorly defined. However, soil chloride levels above about 45 kg/ha in the top 60 cm of soil have been indicated as adequate for near maximum yield of hard red spring wheat (*Triticum aestivum* L.). Continued research is needed in this area and will undoubtedly better define the needs for soil testing and fertilizer application of this micronutrient.

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Chapter 11

Testing Soils for Toxic Metals¹

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The toxic metals Cd, Cr, Hg, Ni, and Pb present a wide range of properties, characteristics, and problems with respect to soil testing and plant analysis. Cadmium, Hg, and Zn form the group IIb elements. These elements have filled inner d orbitals and outer s orbitals. Oxidation states in excess of two are not observed. Chromium and Ni are transition metals; Pb is in group IVa with Si, Ge, and Sn. A discussion of these toxic elements as a group in soils is difficult because of their chemical differences. However, their origin and distribution in soils, uptake by plants and toxicity to plants, animals and humans allows their collective discussion. All of these toxic metals are economically important and are used by people in substantial quantities, providing the possibility of soil and plant contamination from anthropogenic activities such as mining, smelting, and waste disposal, in addition to contributions from mineral weathering of parent materials.

Many of the issues and concerns involved with toxic and potentially toxic materials in the soil, plant, animal, and human environment have been discussed by Baker and Chesnin (1975). Cadmium, Hg, and Pb are toxic to animals and humans, making their behavior in soils and plants of principle importance in relation to food chain contamination (Baker et al., 1979). Chromium can be toxic to plants in its common oxidation states, Cr(III) and Cr(VI) (Mortvedt & Giordano, 1975; Bartlett & James, 1979). The Cr(III) cation is normally the form found in plants and is essential for human nutrition (Huffman & Allaway, 1973). Chromium(VI) is anionic, mobile in soils (Artiole & Fuller, 1979) and waters, and toxic to aquatic life, microorganisms, and animals (Ross et al., 1981; Northeast Regional Res. Publ., 1985). Hexa-

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valent chromium is also a suspected human carcinogen. The relative contribution of Cr(III) and Cr(VI) to plant Cr is not known, but is presumably dependent on soil conditions. Elevated levels of Ni are of concern in soils primarily for phytotoxicity reasons (Soane & Saunderson, 1959; Webber, 1972). Nickel is a required trace element for animal and human nutrition, and most background levels in soils and plants are of little concern for human health (Welch & Cary, 1975) since inhibition of plant growth and development by excessive Ni places a limit on Ni entering the food chain.

One or more availability indices is usually recommended to evaluate potential plant uptake of the toxic metals, although availability and plant uptake can change with environmental and biological conditions. Analysis of soil solution or soil water extracts for the toxic metals in the absence of waste additions or enrichments generally result in concentrations below the $\mu\text{g/kg}$ range. Although these levels may be of chemical interest, both analytical difficulties and lack of correlation with plant uptake data may limit the agronomic value of soil solution analysis for these metals. Exceptions may exist for Cr(VI) and Hg for which sensitive methods are available and for which potential movement and toxicity in groundwater are of concern.

There are many methods available for analysis of the toxic metals (American Public Health Assoc., 1985; Assoc. of Official Analytical Chemists, 1980; Page et al., 1982; USEPA, 1979b). Because levels of Cd, Cr, Hg, Ni, and Pb are often low in soils, care in sampling and handling soil is required. An aluminum sampling tube or one constructed of another material, if tests prove negative for the metals of interest, may be used to obtain soil samples. Selected composite samples should be mixed in an acid washed container and placed in polyethylene bags (Baker & Amacher, 1982). For Cr(VI) analysis, soils should not be dried (Bartlett & James, 1979). For other metals, soils may be air dried in a clean environment if the test method is not sensitive to the drying process. Samples to be analyzed for Hg must be dried below 50°C and must not be exposed to laboratory atmospheres or other areas polluted with Hg, which can be absorbed by soils (Andersson, 1979). Samples should be sieved through a 20-mesh nylon or polyethylene sieve and returned to their original bag (Baker & Amacher, 1982).

Behavior of these metals may be differentiated in soils because Hg will be less prone to adsorption by soil minerals owing to the stability and solubility of its chloride and hydroxide complexes, although organic soil components may retain Hg (Andersson, 1979). Lead and Cr(III) are readily precipitated. Chromium(VI) may be formed or persist at low levels despite being metastable over much of the soil system redox range, and Cd, owing to its bioactivity, complexation with organic matter and mineral surfaces and formation of stable ion-pairs is most sensitive to changes in the chemical environment of the soil (Pickering, 1980). A more general review of these and other elements, referred to as heavy metals, in soils has recently been published (Alloway, 1990). The numerous differences among these toxic metals necessitates some discussion of each metal individually, but where practical they will be considered as a group.

I. CONSIDERATIONS WHEN TESTING SOILS FOR TOXIC METALS

A. Source of Metal

When testing soils for toxic metals one should consider the source of the element. Although a single source at any one location is unlikely, the dominance of one source is quite possible. Background levels may be dominated by soil mineral or parent material composition, while industrial wastes or other sources may govern toxic metal characteristics in soils with elevated levels. For example, Cd levels may be elevated as a result of long-term P fertilization, but are dependent upon the phosphate rock source (Mulla et al., 1980; Mortvedt, 1987). If minerals or parent materials are the major source of a toxic metal to a well-developed soil, we may expect that a steady state has been achieved, which may continue as long as new environmental or cultural conditions are not imposed (e.g., tillage operations, lime application to change rather than maintain pH or irrigation). Examples of mineral contributions to soil toxic metals include soils developed over serpentine deposits that are high in Cr and Ni (Soane & Saunder, 1959; Proctor & Woodell, 1975), or cinnabar deposits (and mine tailings) contributing to high Hg background levels (Harsh & Doner, 1981; Lindberg et al., 1979). Other sources of Hg to areas with elevated levels or to the global Hg pool may include smelters, coal-fired plants (Crockett & Kinnison, 1979), urban areas, waste disposal sites (Andersson, 1979), and geothermal areas (Phelps & Buseck, 1980). Zinc deposits and areas surrounding Zn mine sites are often high in the associated element Cd (Baker & Bowers, 1988). Some shale-derived soils (Lund et al., 1981; Peterson & Alloway, 1979) and phosphate mine sites (Hutchison & Wai, 1979) also contain sufficient Cd to cause elevated levels of plant Cd. Cadmium migration under prevailing soil conditions has been demonstrated at smelter sites with long histories of metal additions (Kuo et al., 1983), and migration may also be inferred from an inability to completely recover Cd after 11 yr of sludge addition (Hinesly et al., 1982a). Galena is the major Pb-bearing mineral, and is common enough to constitute a significant mineral source of Pb to soils (Colbourn & Thornton, 1978; Palmer & Kucera, 1980). Lead-enriched fuels and paints have also contributed to Pb in soils of many areas.

When mineral forms of a toxic element predominate in soils, soil chemistry may be clarified because the chemistry of minerals is relatively well known, and mineralogical methods to determine the contribution of mineral forms to the total soil content are available. The behavior of the fraction of a toxic metal no longer in its mineral form presents a more difficult, but typical, problem in soils. The initial identification of an element's source is important because some soils with a high ore content may have amounts of toxic metals higher than that of soils contaminated with the same metals in other forms, but produce plants with similar metal content. A statistical method to distinguish between contaminated and noncontaminated soils (Davies, 1983) may be useful in identifying problem sites. Fractionation of metal forms

in soils, as well as documentation of source differences and relative effectiveness of extractants, has been reported by several authors (Cd, Pb [Farrah & Pickering, 1978; Miller & McFee, 1983; Harrison et al., 1981]); (Hg [Harsh & Doner, 1981; Lindberg et al., 1979; Hogg et al., 1978b]); (Cr, Ni [Shewry & Peterson, 1976]); (Cd, Ni [Soon & Bates, 1982; Hickey & Kittrick, 1984]).

1. Elemental and Ionic Forms

Although not a common form for toxic elements in soil or soil amendments (with the exception of Hg^0 vapor), if an element is added or still present in the elemental form, considerable chemical literature regarding solubility and possible reactions and their rates at various pH and redox levels becomes useful. Studies using laboratory columns and metal salts to examine the mobility of Cd and Ni (Tyler & McBride, 1982b) and Pb and Cd (Singh & Sekhon, 1983) in soils have shown all these metals to be mobile ($\text{Pb} < \text{Ni} \leq \text{Cd}$). These observations agree with hydroxide precipitation or oxide adsorption of the metals (Tyler & McBride, 1982b), although many mechanisms may be active in the adsorption of metals by soils (Harter, 1979).

2. Organic Forms

The common practice of adding municipal and industrial sludge materials to soils often results in toxic metals in an organic form being added to soils. One of the larger sources of high Cr organic wastes is the leather tanning industry, which may be producing 281 000 Mg yr⁻¹ according to an estimate by Dawson (1978).

Although specific characterization of organic-toxic metal complexes is difficult, some generalizations regarding the behavior of these organic materials are possible. The soil microbial population is responsible for organic-toxic metal material decomposition and constitute a major influence on the chemistry of toxic metals in soil. Some organic-metal complexes (such as methyl mercury) may be directly absorbed by plants and microorganisms and may make a significant contribution to the toxic metal content of biological systems (Czuba et al., 1981). Humic materials can decrease ionic activities by complexing with metals and possibly reduce plant uptake of toxic metals (Tyler & McBride, 1982a; Brady & Pagenkopf, 1978). In addition, the existence of soluble toxic metal chelates in soil may decrease (Elliott & Denny, 1982) or increase (Chubin & Street, 1981) metal sorption depending on soil conditions (pH, mineralogy, and oxides of Fe and Al), and presumably affect metal mobility in soils (Stevenson & Welch, 1979; Welch & Lund, 1987). Although high soil pH may reduce plant uptake of toxic metals (Adriano et al., 1982), the related increased retention of toxic metals by soil metal oxides (Kuo et al., 1985; Abd-Elfatt & Wada, 1981) is of equal or greater importance. Mercury appears to be an exception as it has a particular affinity for, and is retained by, soil organic matter (Zyrin et al., 1981) even at low pH (Andersson, 1979).

The contribution of organic toxic metal complexes to the total soil load of a toxic metal is difficult to determine and may vary with soil and organic type (Petruzzelli et al., 1981). Within a short time following waste application, estimates of the organic portion of the soil toxic metal load may be made from a knowledge of the organic content and organic decomposition rate of the waste material in soils (Wiseman & Zibilske, 1988). In the absence of this information, or after longer periods following application, estimates of organic forms of toxic metals can be made either by selectively extracting the metal from organic materials or by breaking down organic materials in soils and determining the quantity of released metals. The selective extraction method may either employ a metal that is strongly complexed by organic materials and competes for binding sites with toxic metals, or an organic chelate that strongly binds the toxic metal of interest and can be employed to compete with the organic materials in soil for the metal. The chelate extraction method may be employed using two theoretically different but functionally similar procedures. These approaches are discussed in the methods section.

The organic matter destruction approach encompasses many different analytical methods but all involve chemically or physically altering the soil organic matter. High temperature ashing or low temperature ashing in an enriched O₂ environment effectively destroys the organic materials but may also oxidize, dehydrate, or otherwise change the mineral components of soils. The chemical approaches usually employ oxidizing agents such as hydrogen peroxide or hypochlorite to accomplish organic matter destruction, making them similar to the dry oxidation methods. Methods of altering or selectively extracting organic materials in soils are also available and have been described by Schnitzer (1978, 1982). An extractant that is not specific for organic metals may be used prior to and following organic matter destruction; the difference being attributed to organically bound metals.

These methods may be useful to define the organically bound pool of metals in a soil, but the distinction between the native metal-organic pool and the pool because of waste addition cannot normally be made. Because of microbial and plant modification of the organic matter pool, this distinction is no longer meaningful unless a synthetic organic component remains important among the compounds formed biologically in the soil and original sludge material. This may be the case for chlorinated hydrocarbons, and other refractory organic molecules.

The net rate of release of organically bound toxic metals is dependent on many factors, among which are their toxicity to soil microbes, the availability of additional organic materials with which they may become complexed, temperature and other environmental and cultural conditions in the soil environment. The fate of these released toxic metals is not clear, but possibilities include movement in the soil profile, increased plant and microbial uptake, sorption by clays or metal oxides, and "reversion" into either mineral or organic forms (Giordano et al., 1979).

3. Air and Water-Borne Depositions

Air and water-borne deposits may be in the organic or elemental form, but are most likely to be metal oxides or other mineral compounds. Deposits left by air and water streams have distinct downstream patterns, generally with the concentration inversely proportional to distance from the source. If remedial action is required, definition of the areas and estimation of the severity of toxic metal effects are necessary. The materials deposited from plumes are generally sorted by size, and the toxic metal concentration pattern can be uneven and without distinct boundaries. The chemical form(s) of the deposited toxic metal is (are) likely to be uniform over the contaminated area, with differences among sites because of environmental and particle-size differences. An example of a nonhomogenous pattern may be found in Pb distribution along highways (Fergusson et al., 1980). Additional considerations may also apply in some cases. For example, air-borne Hg deposits that result from mercury volatilization (Hg^0) may be more easily revolatilized and thus have greater effects on organisms than equal amounts of particulate mineral forms.

B. Distribution of Metals in a Geographic Region

1. Discrete Area

Discrete areas of toxic metal concentration, with relatively sharp boundaries, are generally characteristic of recent or intentional additions. Organic forms of toxic metals in sludges are most often intentionally applied to a defined and often previously surveyed land area. Toxic metal distribution from these means normally provides adjacent areas without metal applications that may be available for comparison. Although areas adjacent to waste application sites frequently differ in cultural histories, application sites may be compared to surrounding areas, monitored as a unit, and possibly require remedial action or isolation. Waste application sites generally have had uniform past management practices, and allow more options for future supervision. When sampling soils from a discrete area contaminated with toxic metals, a small survey of the area is probably sufficient to establish the current conditions, and subsequent sampling and monitoring can probably be done on a small number of composite samples (provided the area proves uniform). Depending upon the extent of contamination and the potential for further environmental degradation, remedial action may involve soil amendments such as organic matter and lime to reduce metal availability, dedication of the site to waste disposal or other low-risk use, or isolation of the site from humans or animals at risk from exposure to the toxic metals. Among the options available for sites that do not need to be isolated are selection of crop species, cultivars, cultural practices, and the ultimate disposition of the crop to minimize health impacts. An alternative to isolation is removal of the site from agricultural production, and dedication to forestry or park woodland resource.

2. Contamination Halos

In cases where distinct boundaries of toxic metal accumulation are not observed, presumably resulting from anthropogenic sources or dispersion of natural concentrations arising from igneous intrusion or mineral deposition, additional problems are presented. For either anthropogenic or natural sources of a toxic metal a decrease in metal concentration away from the source, and in a direction and pattern that results from the force dispersing the metal must be expected. This plume shadow area may require extensive sampling to describe its size, shape, and concentration distribution of metals. When the source of metals are known, the sampling may be simplified by knowledge of the methods of distribution: wind, water, gravitational, or other important means under the prevailing conditions. For those sources that have not been identified, their identification is often more difficult, as long periods of time and major changes in environmental conditions may have occurred over the period of plume formation. Definition of the extent and increment of added metals, especially if the source of the metal has not been identified, may require many samples and significant analytical expense, although more limited efforts may also be useful (Miller & McFee, 1983). The deposited plume may cover large areas and include an array of environmental conditions, cultural practices, natural or synthetic disturbances and topographical features. In general, more extensive monitoring, and a greater number of rehabilitational alternatives are required when a concentration gradient, halo, or plume pattern is present.

C. Nature of Toxic Hazard

1. Direct Soil Ingestion

Human and animal consumption of metals can occur directly from soil materials ingested intentionally or as a consequence of food contamination. The importance of direct ingestion of toxic metals in soil materials is greatest for those elements acutely toxic to, or chronically accumulated by, animals and humans. In contrast, toxic metals that are selectively taken up by plants are most likely to accumulate and concentrate relative to other elements in the food chain. Toxic elements accumulated by plants in small amounts, but present in soils at potentially dangerous levels, may pose their greatest risk from direct ingestion. Of the five toxic metals considered here, Pb is the element most likely to pose such a threat. Soil particulates acquired through direct soil ingestion or dust inhalation by grazing animals (Thorton, 1974) or playing children probably constitutes the greatest health hazard from soils high in Pb. Roadside and inner city area soil and dust have been shown to be particularly high in Pb and Cd (Harrison et al., 1981). Surface contamination of plants by soil materials or aerosol particulates may constitute a major source of Pb in plant materials (Palmer & Kucera, 1980), and thus in the food chain.

Human consumption of soil is most frequently a problem for young children who play in soil and accidentally or intentionally ingest soil materi-

als. Garden soils in urban or other high metal areas may present health problems as a result of several pollutants at one site (Preer, 1985). Among the factors contributing to metals in garden soils are their proximity to the source, e.g., leaded fuels, lead paint chips, industrial aerosols, and the addition of metals in domestic or industrial sludges and composted organic materials containing high metal materials such as Pb-rich newsprint (Elfving et al., 1979). Combinations of these sources may provide the same individuals with a consistent supply of metal-enriched vegetables and the possibility of direct ingestion of soil materials.

2. Plant Uptake and Food Chain Contamination

Elements or materials that are selectively accumulated or particularly hazardous to humans, but less so to plants, present their greatest health risk through the food chain. Cadmium and Hg fit the pattern of food chain contamination well. Their potential toxicity to humans is great in comparison to their effects on plants. Cadmium is probably of most widespread concern, as it is readily accumulated from soils by plants and may thereby enter the food chain (Chang et al., 1983) and accumulate in animals (Williams et al., 1978; Baker et al., 1979). Levels of plant Cd that cause concern in the food chain usually occur before plant toxicity responses are observed (Kelly et al., 1979; Miles & Parker, 1979b). Cadmium concentrations are generally greater in root than vegetative and leafy plant parts, which in turn are greater than seed portions (Jastrow & Koeppe, 1980; Peterson & Alloway, 1979), except in accumulator species such as Swiss chard (*Beta vulgaris* L.) (Kuo et al., 1985). Concentrations in plants may also be dependent on variety or hybrid within a species, form of Cd in the soil (Hinesly et al., 1982a, b; Street et al., 1977) and soil temperature (Giordano et al., 1979). Presumably plants can selectively partition Cd out of new generation materials (Chang et al., 1982). The extent of partitioning of Cd out of seed portions of crops may be of significance for the important grain crops of the world (Jastrow & Koeppe, 1980). This does not mean that levels of Cd high enough to be of health concern cannot occur in grain and seed portions of plants (Williams et al., 1978; Re et al., 1983).

Mercury may be accumulated by plants either by root uptake or by shoot and leaf absorption of Hg^0 volatilized from soil or present in polluted air (Lindberg et al., 1979). The relative contributions of these modes of uptake are variable, but in certain instances both may be important. Plant roots seem to retain Hg obtained from soil, while aboveground plant content arises largely from atmospheric Hg (Hg^0 vapor or particulates). However, mushrooms (*Agaricus bisporus*) seem to accumulate Hg and present potential problems since high Hg levels may be found in compost used by the mushroom industry (Loughton & Frank, 1974). The concentration of Hg in plant roots and tops depends both on soil and atmospheric Hg sources and climatic conditions (Elsokkary, 1982). Cappon (1987) reported several forms of Hg in vegetables that vary in relative proportion among species. Factors affecting Hg^0 volatilization from soil include temperature (Lindberg et al., 1979) and

biological activity. Soil Hg content does not appear to be a good indicator of volatility (Rogers & McFarlane, 1979). Mercury seems to be strongly retained by both organic and mineral components of the soil (Kromer et al., 1981), with movement more readily occurring in the vapor phase or with root growth rather than in the solution phase (Hogg et al., 1978a, b).

Chromium added to soils in inorganic forms, especially Cr(VI), is more readily extracted by water (Grove & Ellis, 1980) and accumulated by plants than Cr applied in organic wastes (Mortvedt & Giordano, 1975). This is probably because of greater proportions of the more soluble Cr(VI) (McGrath, 1982). Field studies of short duration with Cr applied in organic wastes (Stomberg et al., 1984; Hemphill et al., 1985) or inorganic additions (Rehab & Wallace, 1978a) failed to show increased plant uptake of Cr. In most cases, but with exceptions (Czuba & Hutchinson, 1980), the Pb and Cr found in plants is largely accumulated and partitioned in plant roots (Shewry & Peterson, 1974; Cary et al., 1977; Huffman & Allaway, 1973). In the case of Pb, elevated root levels may be exaggerated because of surface contamination by soil materials. Exceptions to root partitioning of Pb may occur on organic soils (Czuba & Hutchinson, 1980).

3. Plant Toxicity

A third form of heavy metal hazard is plant toxicity. Among the toxic metals considered here, Cr and Ni are the most phytotoxic under prevalent soil conditions. The hexavalent forms of Cr are believed to be deleterious to humans, most mobile in soils because of their anionic form, and probably the form most readily accumulated by plants. The difficulty of demonstrating the form most readily absorbed by plants is related to the interacting complexities of the solubility, redox, pH and microenvironment of the plant root, which determine plant availability of Cr. Combining redox and pH values into a single term ($pe + pH$) as advocated by Lindsay (1979) may help overcome some of these difficulties. Elevated levels of plant Ni are generally not a human nutrition problem because phytotoxicity prohibits excessive plant content, although tolerance by some plant species have been observed for soils enriched with Ni and Cr (Shewry & Peterson, 1976). When equal soil concentrations of the metals Cd, Cr, Ni, and Pb are compared (Dijkshoorn et al., 1979), Ni and Cr seem to be the most phytotoxic, although Mitchell et al. (1978) reported that Cd is more phytotoxic than Ni. The extent of metal accumulation in plants and the order of metal phytotoxicity based on plant content is species dependent, but when comparisons are based on natural or expected abundances of the elements in soils, Ni more often limits plant growth.

Suggested tolerance levels of toxic metals in soils, plants, animal feeds, the human diet, and drinking water are presented in Table 11-1. The maximum concentration of toxic metals in wastes presumed to be acceptable for application of waste materials to soils may also be found in the Northeast Regional Publ. (1985).

Table 11-1. Suggested tolerance levels for toxic metals in soils, plants, animal feeds, foods, and primary drinking water.†

Toxic metal	Maximum cumulative soil levels‡	Plant concentration	Animal feeds	Dietary tolerance	Primary drinking waters§
	kg ha ⁻¹	mg kg ⁻¹		μg d ⁻¹	mg L ⁻¹
Cd	2.5-5.0	1	0.5	≈ 65	0.010-0.005¶
Cr	112-672	2	3000		0.05
Hg	0.9-2.2	0.04	2		0.002
Ni	11.2-67.2	3	50		
Pb	112-672	10	30		0.05

† Northeast Regional Research Publ. (1985) except as noted.

‡ Maximum loading dependent upon soil texture.

§ USEPA (1975).

¶ Commission of the European Communities (1978).

II. SELECTING APPROPRIATE SOIL TEST METHODS

Many factors may be active in the process of retention, and conversely the release of a metal from soil. Among the important factors are ion competition for metal retention sites, metal species and concentration, soil chemical and mineralogical composition and surface area, dissolution of metal hydroxides by proton addition, formation of stable solution complexes and the kinetics of dissolution and precipitation (Harding & Healy, 1979; Pickering, 1980). Additionally, displacement depends on the concentrations and relative affinities for the soil surface of the ions involved and the pH and ionic strength dependence of complex formation (Pickering, 1980).

Dilute extractants such as water and neutral salt solutions are usually too weak to remove a substantial amount of a metal, or to provide an estimate of the buffering or replenishment ability of a soil for the element of interest. However, they may provide an estimate of the availability and perhaps of the amount retained on exchange sites. Conversely, strong extractants such as mineral acids may change soil conditions greatly and dissolve soil minerals so that the extracted amount of a metal has little relationship to that portion of soil metal removed by plants (Palmer & Kucera, 1980). Information provided by both types of analyses may be helpful to evaluate the metal status in soils. To more accurately predict plant and soil response to toxic metals, several levels of metal addition and extracts with a range of displacement abilities can be employed (McBride et al. 1981).

For those nutrients and metals that are complexed by chelating agents, soil extraction by a strong chelate may remove a larger quantity of metal than a crop, but still closely represent plant uptake of metals from soils. The amount of metal removed from a soil by a chelator is dependent on soil and extractant characteristics, many of which can be measured or controlled. Chelate soil tests have been employed to evaluate plant availability for all of the toxic metals, but with varying success. For Cd, Pb (Sadiq, 1983) and Cd, Ni, and Pb (Baker, 1973; Baker & Amacher, 1981) encouraging results

have been found, especially when additional soil characteristics are considered. The mineral stability and slow kinetics of Cr dissolution and the relative instability of Hg chelates lessens the utility of chelate soil tests for these metals. The difference between the chelate-extracted quantity and plant uptake might in part be accounted for by soil conditions, root-soil contact, and extent of root exploitation of the soil profile. Plant roots generally exploit a smaller portion of the soil volume than an extraction solution, but the portion of the soil in close contact to plant roots may be substantially depleted. These factors could be especially important when comparisons are made among species and across sites since both soil and crop conditions may contribute to differences in plant uptake.

Metals associated with organic materials may be extracted with the same techniques used for other soil materials, or an approach using a strongly bound metal to compete for organic-binding sites may be employed. The competing metal approach most often employs Cu, a metal known to bind strongly to organic materials, and thereby displace a suite of metals previously present on the mineral and organic matter surfaces. To the extent that Cu or any other selected metal is specific for organic surfaces, this approach is both logical and useful. Cadmium, Ni, and Zn extracted with 0.125 *M* Cu(II) acetate was shown to be significantly correlated with soil organic matter content (Soon & Bates, 1982).

The USEPA (1979a) recommended a strong acid extraction for sediments. This method has been used to compare untreated soils with comparable soil samples from locations treated with sewage sludge or other wastes. The method provides results for total sorbed metals, which includes the nonvolatile metals within the nonsilicate fraction of the soil. By comparing untreated and treated soils, a measure of the total loadings of Cd, Ni, Pb, Cr, and other nonvolatile metals is obtained. This method with some revisions has more recently been made an official method for sediments, soils, and sludges (USEPA, 1986).

Other commonly used methods for Cd, Pb, and Ni include dilute HCl (0.1 *M* HCl) and double acid (0.05 *M* HCl and 0.0125 *M* H₂SO₄) extractants (Cox & Wear, 1977; Korcak & Fanning, 1978). A rapid method for detection of Pb-contaminated soils is also available (Preer & Murchison, 1986). Methods for soil Cr determinations generally may be divided into soluble Cr(VI), organic Cr forms and total Cr tests. For Hg, total, soluble and perhaps volatilizable fractions (Cannon & Dudas, 1982; Dudas & Cannon, 1983) are the options for testing soils. Lead isotope ratios may be used as an aid in identifying the sources and relative contribution of anthropogenic Pb to soil (Gulson et al., 1981).

There are many instrumental techniques available for analysis of toxic and trace metals. Among the most commonly employed methods are flame and furnace atomic absorption spectrophotometry (AAS), inductively coupled Ar plasma spectroscopy (ICP), and cold vapor analysis for Hg (American Public Health Assoc., 1985; Assoc. of Official Analytical Chemists, 1980; Page et al., 1982; USEPA, 1979b). Anodic stripping voltammetry and polarographic techniques are sensitive methods for quantification of many

elements, and thus may be considered as optional methods of toxic metal analysis (Street & Peterson, 1982).

Soil and mineral standard reference materials are available from the National Bureau of Standards, U.S. Dep. of Commerce. These materials are essential to assure the quality of results produced by analytical methods for total element content of samples. Reference materials for use with soil test methods to determine available or extractable metals are generally not commercially obtainable. Any time a test method is used frequently in a laboratory, one or more soils should be selected and developed as an in-house reference material by repeated analyses for use in checking accuracy and precision of the soil test. In addition to laboratory check samples, a periodic exchange of samples among several laboratories employing the method of interest should be used to check for systematic errors and calculation or interpretation differences. For analysis of toxic and other metals, laboratories are urged to follow the USEPA (1979c) quality assurance/quality control procedures.

A summary of some of the extractants used to test soils for toxic metal content and influence on plant composition is presented in Table 11-2. These citations are not meant to be comprehensive, but illustrative, and additional examples are readily available in Page et al. (1982), the text and bibliography of this review or in current issues of many environmental journals.

III. SOIL TESTING METHODS

A. Chelate Extraction Method

The approach pioneered by Norvell and Lindsay (1969) and applied in soil testing by Soltanpour (1985) and Lindsay and Norvell (1978) involves the use of chelates in the 0.01 *M* range as extractants, with resulting extraction levels correlated to biological response in the soil system. Lindsay's method remains one of the more commonly employed, although that of Soltanpour (1985) is probably quicker and more easily adapted to routine testing. The approach pioneered by Baker (Baker, 1973; Baker & Amacher, 1981) involves lower levels of chelate intended to cause less perturbation of the system and invoke a small exchange of metals with the soil surface. Baker's method (Baker & Amacher, 1981) and the approach of Fujii et al. (1983) both employ iterative calculation of metal ion activity values in soil. Both methods include the effects of pH and other metals on the stability of the chelate complex and the ion activity, theoretically making them applicable to a wider range of soil, environmental and plant conditions. Fujii et al. (1983) employed a second extract to accurately fix CdCl_2 activity. All chelate approaches may be thought of as extractions to a fixed metal-chelating sink, meaning that the extractant capacity and metal-chelate affinity for all soils is fixed upon selection of a chelate and its concentration. The primary differences between these methods are in subsequent calculations and interpretation. The method of Baker has been applied extensively for mine soil and

Table 11-2. Summary of selected extractants for toxic metals in soils and plants for which correlation is reported and citation.

Extractants	Elements	Plants	Reference
NTA, H ₂ O, HCl + AlCl ₃ , EDTA, DTPA, CH ₃ COOH, CH ₃ COONH ₄ , HNO ₃ + HCl, (COOH) ₂ + (COOHN ₄) ₂	Cd, Cu, Ni, and Zn	Swiss chard (<i>Beta vulgaris</i> L.)	Haq et al., 1980
1 M KCl, 2 M HNO ₃	Cr	Corn roots (<i>Zea mays</i> L.)	Hafez et al., 1979
0.42 M CH ₃ COOH, 0.002 M CaCl ₂ , 0.05 M CaCl ₂ , 0.05 M EDTA	Cd	Sorption isotherms	Jarvis & Jones, 1980
Total analysis	Hg	Rice roots (<i>Oryza sativa</i> L.)	Morishita et al., 1982
Total, weak acid, CH ₃ COONH ₄	Cr, Ni	Many	Proctor & Woodell, 1975
Bray P ₁	Pb	Soybean [<i>Glycine max</i> (L.) Merr.]	Miller et al., 1975
CH ₃ COONH ₄ + CH ₃ COOH (pH 4.8)	Pb	Six vegetables	Nicklow et al., 1983
Total (added as sulfate salts)	Cd, Ni	Cotton (<i>Gossypium</i> sp.)	Rehab & Wallace, 1978b
Total (x-ray fluorescence spectroscopy)	Pb	Five vegetables	Spittler & Feder, 1979
DTPA	Cd, Cu, Pb, and Zn	Various	Miles & Parker, 1979a;
0.5 M NaHCO ₃ , 1 M CH ₃ COONH ₄ , total analysis	Hg	Alfalfa (<i>Medicago sativa</i> L.)	Baker & Bowers, 1988 Lindberg et al., 1979

spoil reclamation (Baker & Buck, 1988); land application of sewage sludges (Shipp & Baker, 1975) and more recently for "clean-up" and human food chain Cd evaluations for a USEPA super-fund site (Baker & Bowers, 1988). The method has been described (Baker & Amacher, 1981), but it requires appropriate computer software for calculating and interpreting the laboratory results.

The method of Norvell and Lindsay (1969) is described in the following section. The methods cited above and other methods employing a variety of organic chelates may be used, provided data for interpretation of the results are available. Buffering the extract solution to pH 7.3 with triethanolamine (TEA) reduces the dissolution of minerals and release of trace metals by proton exchange. Calcium chloride is included to minimize effects of CaCO_3 dissolution in soils containing free carbonates. All glassware used for the extraction, filtration, and storage of extracts should be acid soaked and thoroughly rinsed in high-quality deionized water.

1. Reagents and Procedures

Diethylenetriaminepentaacetic acid (DTPA) extracting solution—To prepare 1 L of this solution, dissolve 14.9 g of reagent-grade TEA, 1.97 g of DTPA, and 1.47 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in about 200 mL of deionized water. After dissolution, dilute to 900 mL and adjust the pH to 7.3 with 1 M HCl while stirring, then complete the dilution to 1 L. The resulting solution is 0.005 M DTPA, 0.01 M CaCl_2 , and 0.1 M TEA.

To 10 g of air-dried soil in a 125-mL flask, add 20 mL of the DTPA solution. Cover with plastic stoppers and shake at two cycles s^{-1} for exactly 2 h. Gravity filter the suspension through Whatman no. 42 or equivalent filter paper. The shaking time is critical as the extraction is not complete, and metals will continue to dissolve if left for greater periods. Standards should be prepared in the extracting solution by adding appropriate volumes of 1000 mg L^{-1} of stock standards prior to final dilution of the extracting solution. Analyze the filtrate for Cd, Ni, and Pb or other elements of interest by AAS or ICP.

2. Interpretation

The results of trace metal analysis are most commonly expressed as mg kg^{-1} on a soil dry weight basis. This is equivalent to ppm in the soil, and can be obtained by multiplying the solution concentration by 2. If other units are used, especially volume-based units, then the methods used to obtain those units and conversion factors to express results on a weight of soil basis should be included. Suggested approaches for reporting soil test results have been published (Dahnke, 1988).

B. Dilute HCl Method

Dilute HCl as a soil extractant, relating soil-extractable Zn levels and titratable alkalinity to available Zn was described by Nelson et al. (1959).

They reported that for a range of calcareous and high pH noncalcareous soils the combination of extractable Zn and alkalinity predicted the crop Zn status. Although similar success has not been demonstrated for toxic metals, a dilute HCl extract may correlate well with the total metal content of the soil, and under some conditions, plant uptake. As with total metal analyses, other soil parameters must be considered to estimate plant available amounts of toxic metals. Among these parameters are organic matter content, clay content, soil pH and silicate and nonsilicate minerals present.

1. Reagents and Procedures

Prepare 0.1 *M* HCl solution by diluting 1 volume of redistilled 6 *M* HCl with 59 volumes of deionized water.

Add 20 mL of 0.1 *M* HCl to 2.00 g of soil in a 30- to 50-mL centrifuge tube. Cover, shake for 5 min at two or greater cycles s^{-1} , uncover, and centrifuge until a clear supernatant is obtained. Decant the supernatant and repeat the extraction two or more times until the equilibrium solution pH is <2.0 . Adjust the combined extracts to 100 mL final volume and analyze the mixed solution for Cd, Cr, Hg, Ni, and Pb or other metals of interest using AAS, ICP, or cold vapor (for Hg) detection. Standards should be prepared in the extracting solution by adding appropriate volumes of 1000 mg L^{-1} stock standards prior to final dilution of the HCl to 0.1 *M*.

2. Interpretation

There are many variations of the 0.1 *M* HCl method and unless a specific method is carefully followed, the results of analyses may not be comparable. The critical factors are: the final solution pH is below 2.0, a minimum of 15 min soil-solution contact time is obtained, and that at least two cycles s^{-1} shaking is observed. This method has been reported as a single extraction method, but on high pH soils cation exchange converts the extractant to the equivalent of approximately 0.05 *M* $CaCl_2$. A final pH of 2.0 must be obtained.

C. Double Acid Method

The double-acid method has been developed for use on soil with low CEC, low pH, and low levels of organic matter. Comparisons of results for the double-acid extract, the dilute HCl method and the DTPA method have been made (Wear & Evans, 1968). When the method is applied to soils that fit the conditions under which it was developed then the results may be equally as useful as other methods of predicting metal availability. Additional soil parameters, as for the other toxic metal tests, should also improve the reliability of this test.

1. Reagents and Procedures

Dilute 16 mL of 6 *M* redistilled HCl and 1.4 mL of concentrated sulfuric acid to 2 L with deionized water.

To 5 g of air-dry soil, add 25 mL of the extraction solution in an acid-washed 50-mL flask and shake for 15 min at three cycles s^{-1} . Filter the solution through Watman no. 42 or equivalent filter paper. Standards should be prepared in the extracting solution by adding appropriate volumes of 1000 $mg\ L^{-1}$ stock standards prior to final dilution of the extracting solution. Analyze the filtrate for Cd, Cr, Hg, Ni, and Pb or other elements of interest using AAS, ICP, or cold vapor (for Hg) detection.

2. Interpretation

Comparison of the double-acid extract with DTPA have shown each to provide superior correlations with plant uptake under some conditions, but found DTPA to be superior over a wider range of soil conditions (Korcak & Fanning, 1978).

Some of the problems and potential sources of variation in estimating metal available to plants from soil tests are discussed by Barry and Clark (1978). For toxic metals, the extreme natural variation and the additional variation that can be introduced by human activity may require a 50% or more increase over background levels to detect metal enrichment in the soils of an area. For Hg, a budgeting approach that attempts to account for inputs to and losses from a soil may be more sensitive to changes in metal content than soil analysis (Andersson, 1979).

Each soil test is most useful under conditions where the extractable amount of a metal has been related to crop uptake under a particular set of soil, crop, and environmental conditions. These conditions exist where extensive calibration work has been completed for the soil test and regional crops and soils. A test may become more useful if regression equations are available to relate both the extractable level of a metal and the soil pH to crop response. For chelate soil tests, the inclusion of changes in metal availability with pH allow the application of chelate extractions over wider ranges of soil conditions (Korcak & Fanning, 1978). Under more complex, or less studied soil and climatic conditions, one of the chelate soil tests that includes extractable levels of other metals and soil cations may be more useful because it enables more of the potentially important soil factors to be included in an estimate of plant-available metals. Disadvantages of the chelate soil tests include a potentially long equilibration time, greater number of analyses if the interactions of other metals are to be included in the predictive results, and possibly extensive calculations to complete an estimate of the contribution by the soil environment to the availability of the toxic metal of interest.

D. Total Sorbed Metals (From USEPA, 1986)

1. Reagents and Procedures

Concentrated HNO_3 , and HCl, hydrogen peroxide (30%) and American Society for Testing and Materials (ASTM) type II water are required reagents. The acids and oxidant should be analyzed separately to determine the levels of impurities. If the method blank is less than the method detec-

tion limit the acids and oxidant may be used. Reagent grade acids are generally acceptable for flame atomic absorption spectroscopy. However, ultra-pure acids may be needed for graphite furnace atomic absorption spectroscopy.

Add 10 mL of 1:1 HNO_3 to 2 g of air-dry soil, in a 150-mL pyrex beaker and cover with a watch glass. Place the samples on a hot plate and cautiously heat to 95 °C and reflux for 15 min without boiling. Cool the beaker, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 min. Repeat the last step. With the watch glass covering three-fourths of the beaker, evaporate the solution to 5 mL without boiling. Cool the sample, add 2 mL of type II water and 3 mL of 30% H_2O_2 . With the beaker covered, heat the sample gently to start the peroxide reaction. If the effervescence becomes excessively vigorous, remove the sample from the hot plate and cool. Continue to add 30% H_2O_2 in 1-mL increments, followed by gentle heating, until effervescence is minimal. Next, add 5 mL of concentrated HCl and 10 mL of type II water, return the covered beaker to the hot plate and reflux for 15 min without boiling. After cooling, filter the sample through Whatman no. 41 filter paper (or equivalent) and dilute to 50 mL with type II water.

For samples to be analyzed by graphite furnace atomic absorption spectroscopy, do not add concentrated HCl to the sample but continue heating the HNO_3 -peroxide digestate until the volume has been reduced to 5 mL. After cooling, filter the sample with Whatman no. 41 filter paper (or equivalent) and dilute to 50 mL. Standards should be prepared in the appropriate acid mixture for the analysis method by diluting 1000 mg L^{-1} stock standards to the desired final concentrations.

2. Interpretation

This method is not suitable for Hg. For Cd, Ni, Pb, Cr, As, and Se and other trace metals in soils, the method provides a measure of the total concentrations that are exchangeable or adsorbed by soil components. The method does not include trace metals associated with silicates. Therefore, the use of the procedure to measure total metals is not recommended. However, this method is the official procedure used by USEPA for metals in soils and it gives a reliable measure of the amounts of the metals added to soils as nonsilicates from industrial sources.

E. Total Content Analysis of Soil for Chromium, Nickel, and Other Metals

A carbonate fusion (Lim & Jackson, 1982) or lithium metaborate method may be used for total analysis of Cr and Ni. Many sample decomposition methods and potential problems of elemental analysis are described by Bock (1979). Fusion methods are usually unacceptable unless shown otherwise for the volatile elements Cd, Hg, and Pb. For these elements, a low temperature

wet digestion method generally employing $\text{NHO}_3\text{-HClO}_4$ may be used (Lim & Jackson, 1982). For digestion of samples for Pb analysis, the use of H_2SO_4 should be avoided to preclude PbSO_4 precipitation (Burau, 1982).

F. Readily Available Chromium Test

1. Reagents and Procedures

Prepare 0.01 *M* KH_2PO_4 by dissolving 1.36 g of KH_2PO_4 in deionized water. Diphenylcarbazide reagent is prepared by dissolving 0.4 g of *S*-diphenylcarbazide in 100 mL of ethanol, and mixing this solution with a solution prepared from 120 mL of 85% H_3PO_4 diluted to 400 mL with water.

Three grams of fresh, moist field soil are extracted with 25 mL of the KH_2PO_4 solution by shaking for 5 min in a 50-mL centrifuge tube. One mL of the diphenylcarbazide reagent is added to 8 mL of the centrifuged soil extract (diluted if necessary), mixed, and transmittance determined at 540 nm after 20 min. Readily available Cr on a dry weight basis is calculated from the moisture content of a separately dried soil.

2. Interpretation

Interpretation of soil tests for Cr requires consideration of soil redox reactions and of the factors that affect the distribution and transformations of Cr species in soils such as soil Mn coatings, soil organic matter, and soil pH (Bartlett & James, 1979, 1988; James & Bartlett, 1983).

G. Total Soil Mercury

A wet digestion of soil or sediment in a reflux flask using H_2SO_4 and HNO_3 is the approach Stewart and Bettany (1982) recommend. Availability indices are not well developed, but solution extractable amounts and plant uptake or specially constructed incubators capable of measuring Hg^0 volatilization are reasonable possibilities (Rogers & McFarlane, 1979; Lindberg et al., 1979). Alternatively, a method for estimating an allowable soil Hg level has been developed by Bashor and Turri (1986) and may serve as a guide for other researchers.

IV. INTERPRETING SOIL TEST RESULTS

Among the many soil tests that have been used to quantify metals in soils, the selection of a particular test should be based on the usefulness of the information to be obtained. One of the principle factors affecting usefulness and a major justification for selecting a particular test is the availability of good correlation data, both for the soils of the area and for the crop being grown. When such data are available, the selection of that test is usually indicated. If sufficient data is to be collected to allow recorrela-

tion of field results to an alternate test, or cross correlation among several soil tests selected for comparison then other tests may be considered. The use and interpretation of soil tests require knowledge of the extractant, the soil on which it is used and crop to be grown.

Each soil-plant system studied with respect to toxic metals should be independently analyzed and also compared to similar systems (Pickering, 1980). Ultimately, some efforts must be made to standardize methods and select necessary measurements on the soil-plant system to allow description and prediction of the systems behavior. In the interim, well-documented methods should be employed, and whenever possible, the methods selected should be from among a short list with proven value.

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Chapter 12

Testing Soils for Salinity and Sodicity

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The diagnosis, management, and need for reclamation of salt-affected soils are evaluated by measurements of their salinity and sodicity. *Soil salinity*, which refers to the presence of excessive levels of dissolved inorganic solutes, is generally assessed by the electrical conductivity of the saturation extract (EC_e), since EC is a practical index of total ionized solute concentration. *Soil sodicity*, which refers to the excessive presence of Na, is generally expressed in terms of the exchangeable sodium percentage (ESP) or the sodium adsorption ratio of the saturation extract (SAR_e). The latter is more conveniently and accurately determined and these two parameters are closely related.

In this chapter, we present procedures for testing soils for salinity and sodicity; in addition, guidelines are given for diagnostic purposes. Detailed analytical methods for determining the concentrations of the individual salt constituents in waters and soil extracts are described in Rhoades (1982a); and descriptions of alternative methods for determining salinity in the field are described in Rhoades (1984) and Rhoades and Oster (1986).

I. LABORATORY METHODS FOR SALINITY AND SODICITY APPRAISAL

A. Soil Sampling, Storage, and Preparation

1. Soil Sampling

Soil salinity is among the most variable properties of soils, and its variation within a field is generally greater than analytical errors. Thus, the reliability of analytical data for salinity appraisal is often limited by sampling error. Kelley (1922) described it realistically: "It is evident that the analysis of a single soil drawn from one place in the area studied has very little

value. . . If similar variation exists in alkali soils generally, it may be safe to conclude that the analysis of samples such as commonly submitted by practical farmers is a waste of time."

The method of appropriate sampling is dictated largely by the purpose for collecting soil samples and the variation existing within the sampling area. In some cases, we may only want to identify the salinity level at a selected point in a field. If this is the objective, statistical considerations may be academic. In many cases, soil samples submitted for routine analysis come from an area characterized as a "saline area" or a "sodic spot," covering a fraction of a hectare to many hectares within a cultivated field. Such an area may consist of a single soil type or several types, and salinity and sodicity typically vary greatly within such areas. For instance, salinity readings in surface-irrigated orchards in the El Paso Valley of Texas varied two- to threefold within salt-affected areas of < 1 ha (Miyamoto & Cruz, 1986). Even greater variation in salinity was observed in a 0.8 ha fallow field near Bet Dagan (Bresler et al., 1984). The variation in sodicity is usually smaller than that of salinity in irrigated fields (e.g., Miyamoto & Cruz, 1986), but can be large in nonirrigated soils as documented by Sayegh et al. (1958) in the Baker Valley of Oregon. The spatial variations in salinity and sodicity are site specific, and their approximate ranges for applicable soil types, or series, or fields must be known before soil samples can be collected appropriately. This information can be estimated from the much more easily acquired field measurements of bulk soil electrical conductivity (EC_d) made using portable instrumentation.

Once the variability is known, the question is reduced to sampling adequacy. The frequency distribution of salinity in an area consisting of multiple soil types or series often presents a skewed distribution (e.g., Wagenet & Jurinak, 1978; Miyamoto & Cruz, 1986). However, in an area consisting of a single soil type, both salinity and sodicity (on a depth-averaged basis) generally follow an approximately normal distribution (Miyamoto & Cruz, 1986, 1987). Therefore, the number of soil samples (N) required to meet a desired statistical accuracy can be estimated by

$$N = t_{\alpha}^2 SD^2 / (d \bar{x})^2 \quad [1]$$

where t_{α} is the normalized deviate for a given confidence level of α (e.g., $t = 1.96$ at a confidence level $\alpha = 5\%$), SD is the standard deviation, and d is the deviate range from the true mean, \bar{x} . The value for N is site-dependent, and in torrifluvents ranges from 5 to 20 samples per hectare of border or basin irrigated land consisting of a single soil type when d is taken as 15% of the true mean at a 5% confidence level (e.g., Miyamoto, 1988). The numbers of samples required to characterize salinity or sodicity at individual soil depths are usually greater than those required for depth-averaged sampling, owing to greater variation in the former case. Once the number of samples required is determined, soil samples can be collected within an area consisting of a single soil type at random sites or at sites following determined spatial schemes.

When detailed soil maps are not available and soil characteristics are poorly known, an equal-spaced grid pattern can be used for sampling (e.g., Petersen & Calvin, 1965). The data collected in this fashion can be used to describe the spatial distribution of salinity or sodicity over the area through kriging (Hajrasuliha et al., 1980). Such information is useful, for instance, for planning reclamation of saline or sodic soils or for making alternative management decisions. However, this type of spatial analysis generally demands numerous samples and is not usually included in routine appraisals. If the purpose is to obtain the value of the mean salinity of an area, a systematic grid sampling is not nearly as efficient as is a soil type-based sampling system (Sayegh et al., 1958; Miyamoto, 1988).

Soil salinity and sodicity typically vary with depth. Under irrigated conditions, salinity generally increases approximately exponentially with depth in sandy soils and approximately linearly in clay soils to the bottom of the root zone. In clay soils having water infiltration problems or shallow water tables, it is common to observe higher levels of salinity at shallow depths. Soil samples should be collected from that part of the profile from which the plant is extracting significant amount of water by observed horizons in the profile or by arbitrary depth-increments, such as every 30 cm, in the absence of such horizons. The samples collected by arbitrary depth-increments generally show greater spatial variability than those collected by horizons, especially when the thickness of the horizons vary with location within the sampling area.

Salinity distribution patterns are also influenced by the methods of irrigation and cultivation (e.g., Bernstein & Fireman, 1957; Ayers & Westcot, 1985; Yaron et al., 1973). Since high-salt accumulations often occur in the ridges of furrow-irrigated crop beds and at the wetting front surrounding drip emitters, these depths should be avoided or else sampled separately when assessing the salinity hazard to established crops. (These high-salt bands present at the soil surface or the extremities of the crop root zone do not generally harm established crops). The near-surface depth of soil above and surrounding the seeding depth may be collected to assess relevant salt conditions for seedling emergence and establishment (Miyamoto et al., 1985b).

Equipment conventionally used for general soil sampling purposes are satisfactory for sampling saline or sodic soils. Tube samplers are most convenient when composite samples are to be taken. Large diameter samplers generally yield smaller variation in salinity measurements than do small tube samplers (Hassan et al., 1983). It is preferable to sample when the soil is reasonably dry and after all loose plant material and debris are removed from the surface. If a salt crust is present it should be sampled separately, if desired, but in no case allow it to be included in the major soil sample. Care should be taken to prevent dislodgement of an upper layer while collecting the deeper layers when using augers or tube samplers to obtain successively deeper samples. To avoid contamination and to facilitate mixing of the samples, it is advisable to pass each depth-sample through a 0.6 to 0.8 cm screen and thence into a separate plastic bucket. For routine analyses, 200 g (clay soils) to 400 g (sandy soils) of soil are usually sufficient. The samples should be trans-

ferred into plastic, air-tight bags with tags for labeling (preferably placed inside, if the samples are sufficiently dry). All soil samples should be coded for reference. Pertinent field information should be recorded, such as irrigation methods, irrigation water quality, crop condition, soil moisture level, time since last irrigation, and soil permeability (leaching fraction) to help in the interpretation of analytical results.

2. Sample Storage and Preparation

The method of sample storage depends on the duration of the intended storage as well as on whether analyses of pH and Ca and carbonate concentrations are desired. For short-term storage, samples can be stored in a cool room or, if available, in a refrigeration unit without drying. Prior to analysis, samples may be air dried to facilitate mixing to obtain a homogeneous sample. For long-term storage, the samples should be first air dried. Prolonged air drying should be avoided, especially under a hot and dry climate, as salts can precipitate and become difficult to dissolve and extract. Likewise, oven drying of soil samples should be avoided. Salts can be extracted without difficulty if samples are processed as soon as they become dry enough to conveniently grind and mix.

Excessive grinding of samples should be avoided. Reduce the clods and large aggregates to <4 mm using a wooden or rubber roller, mallet, or any effective method that will not pulverize the soil particles. Weigh and discard the >4 -mm material. Place the sieved soil on a plastic sheet; mix by repeatedly pulling opposite corners of the sheet to the center of the sheet. Determine moisture content on an aliquot of the sample, and store the rest in a sealed plastic container.

B. Saturation Extract and Other Aqueous Extracts

1. Principles

It is desirable to know the composition of solutes existing in the soil water at field water contents. However, because present methods of obtaining soil water samples at field water contents are not practical for routine purposes, soil solution extracts are generally used. Because the absolute and relative concentrations of various solutes in the extract are influenced by the soil/water ratio (Reitemeier, 1946), the ratio must be specified and it is desirable that it be standardized to obtain results that can be applied and interpreted uniformly. Soil salinity is conventionally defined and measured on aqueous extracts of saturated soil pastes (U.S. Salinity Laboratory Staff, 1954). This soil/water ratio is the lowest practical ratio for which enough extract for analysis can be readily removed from the soil with low pressure or vacuum. It is generally related in a predictable manner to field soil water content. It is quite reproducible, once trained in its preparation. Normal deviations in the ratio do not significantly affect salinity appraisal. Almost all of the salinity crop-tolerance data used to diagnose salinity status is expressed in terms of the electrical conductivity of the saturation extract and relations

used to predict ESP from SAR are also based on the saturation extract (U.S. Salinity Laboratory, 1954; Sposito & Mattigod, 1979; Rhoades, 1982b; Jurinak et al., 1984).

Solutions from more dilute extraction ratios, 1:1, 1:5, etc., are easier to obtain than saturation, but they are not related in as predictable a manner to field soil water contents. Errors from peptization, hydrolysis, cation exchange, and mineral dissolution are enhanced with such extracts. This is particularly true in gypsiferous soils where the dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) significantly affects the concentration of dissolved salts. When relative changes in solute concentrations are to be monitored, these dilute extraction ratios may be used to advantage, but they are not advised for diagnosis purposes.

Once soil extract samples are obtained, laboratory chemical analyses are carried out to determine the EC and the SAR and, if needed, the concentrations of other solutes in the extract.

2. Saturation Extract

Weigh 200 to 400 g of air-dry soil of known water content into a plastic container having a snaptight lid. Weigh the container plus contents. Add distilled water to the soil with stirring until it is nearly saturated. Allow the mixture to stand covered for several hours to permit the soil to imbibe the water, and then add additional water to achieve a uniformly saturated soil-water paste. At this point, which is generally reproducible to within $C = 5\%$, the soil paste glistens as it reflects light, flows slightly when the container is tipped, slides freely and cleanly off a spatula, and consolidates easily by tapping or jarring the container after a trench is formed in the paste with the side of the spatula. After mixing, allow the sample to stand for at least 2 h (preferably overnight) and then recheck it for saturation. Free water should not collect on the soil surface, nor should the paste have stiffened markedly or lost its glisten. If the paste is too wet, add additional dry soil of known weight to the paste mixture. Upon attainment of saturation, reweigh the container plus contents. Record the increase in weight, which is the amount of water added. Calculate the saturation water percentage from the weight of oven dry soil and the sum of the weights of water added and that initially present in the air-dry sample; $SP = 100 (\text{g of water/g of oven-dry soil})$. After allowing the saturated soil paste to stand 2 h or more, transfer it to a Buchner or Richards-type (1949) filter funnel fitted with highly retentive filter paper, such as Whatman No. 42. Apply vacuum, and collect the filtrate in a test tube or bottle. If the initial filtrate is turbid, refilter or discard it. Terminate the filtration when air begins to pass through the filter. Before storage, add one drop of 0.1% $(\text{NaPO}_3)_6$ solution¹ for each 25 mL of extract; alternatively dilute 1:1 with distilled water. This last step can be omitted if the effect of CaCO_3 precipitation upon the composition is negligible.

¹Sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ solutions, 0.1%: Dissolve 0.1 g of $(\text{NaPO}_3)_6$ in water and dilute the solution to 100 mL.

3. Other Aqueous Extracts

To prepare aqueous extracts of soil/water ratios of 1:1 and 1:5, etc. weigh a sample of air-dry soil of appropriate size, and transfer it to a flask or bottle. Add the required amount of distilled water, stopper the container, and shake in a mechanical shaker for 1 h. If a mechanical shaker is not available, shake the container vigorously by hand for 1 min at least four times at 30-min intervals. Filter the suspension using highly retentive filter paper, such as Wattman No. 42. (Discard or refilter the initial filtrate if it is turbid.) Add 0.1% (NaPO_3)₆ solution¹ at a ratio of one drop for each 25 mL of extract.

4. Comments

In the preparation of the saturation paste, it is recommended to record the soil water content at saturation—the so-called *saturation percentage*. This information is useful to estimate soil texture (see Soil Survey Staff, 1951) and the salinity of the soil water at different field moisture levels. Given knowledge of the soil bulk density (ρ_b), the electrical conductivity of soil water (EC_w) at volumetric content (θ_w) may be estimated as: $\text{EC}_w = \rho_b \text{EC}_e \text{SP}/100 \theta_w$ (after Rhoades et al., 1989c). Special precautions should be taken to prepare a saturated soil paste with peat and muck soils or very fine or very coarse-textured soils. If possible, peat and muck soils should not be allowed to dry following collection because their saturation water content changes upon drying. Peat and muck, especially if coarse or woody, require at least an overnight imbibition period to obtain a definite endpoint for the saturation point. After the first wetting, pastes of these soils usually stiffen upon standing. Adding water and remixing then give a mixture that usually retains the characteristics of a saturated paste. One may also experience a similar problem in preparing the saturation paste of Na-rich soils high in clay content. With fine-textured soils, water should be initially added, with a minimum of mixing, to bring the sample nearly to saturation and then allow time for the water to be imbibed. This minimizes the formation of unwetted clumps during the subsequent stirring, speeds the mixing process, and helps attain a more definite endpoint. Care should be taken not to overwet coarse-textured soils. The presence of free water on the surface of the paste after standing is an indication of oversaturation. Even small amounts of free water can lead to significant errors in saturation paste water contents for very coarse-textured soils. Additional soil (of known weight) can be added to the paste in the case of oversaturation to correct this problem. This paste should be remixed and reequilibrated.

Alternative methods of preparing the saturated soil paste have been described by Longenecker and Lyster (1964), who proposed wetting the soil sample on a capillary saturation table; Beatty and Loveday (1974), who recommended predetermining the amount of water at saturation on a separate soil sample using a capillary wetting technique; and Allison (1973), who recommended slowly adding soil to water (oversaturation method). Similar results are obtained with these methods. The choice of method is primarily

one of personal preference. Sonneveld and van den Ende (1971) recommend use of a volume-based extract made up of one part soil and two parts water.

Sodium hexametaphosphate is added to the extract to inhibit the precipitation of CaCO_3 . The amount of $(\text{NaPO}_3)_6$ solution added increases the Na concentration by about 0.5 mg/L, or 0.02 mmol_c/L, which is inconsequential compared with the possible loss of CaCO_3 . A 1:1 dilution with distilled water is an alternative to the use of $(\text{NaPO}_3)_6$ to prevent CaCO_3 precipitation during storage. Thymol can be added to the paste to minimize the effect of microbial activity on saturation extract composition during equilibration (Carlson et al., 1971). The extracts should be stored at about 4°C until analyzed.

C. Determination of Salinity: Electrical Conductivity of Extracts

For this determination, use a direct readout, temperature compensating conductivity meter.

1. Apparatus

- a. Conductivity meter.
- b. Conductivity flow cell with automatic temperature compensation.

2. Regents

- a. Standard KCl solutions, 0.010 and 0.100 *N* solution: For 0.010 *N* solution (1.412 dS/m at 25°C) dissolve 0.7456 g of KCl in distilled water, and add water to make 1 L at 25°C. For 0.100 *N* solution (12.900 dS/m at 25°C), use 7.456 g of KCl.

3. Procedure

Rinse and fill the conductivity cell with standard KCl solution. Adjust the conductivity meter to read the standard conductivity. Rinse and fill the cell with the extract and read EC, corrected to 25°C, directly from the digital display.

4. Comments

Because of marked differences in the equivalent weights, equivalent conductivities, and proportions of major solutes in soil extracts and water samples, the relationships between EC and salt concentration or between EC and osmotic potential are only approximate. They are still quite useful, however. These relationships at 25°C are:

- a. Total cation (or anion) concentration, mmol_c/L $\approx 10 \times \text{EC}$, in dS/m.
- b. Salt concentration, mg/L $\approx 640 \times \text{EC}$, in dS/m
or Salt concentration, mg/L $\approx 740 \times \text{EC}$, in dS/m (gypsiferous soils)
- c. Osmotic potential, bars $\approx 0.4 \times \text{EC}$, in dS/m.

The electrical conductivity of an extract is generally lower than that of the soil solution because of dilution. In the case of the saturation extract, the water content of the paste averages two (ranging from 1.8–2.5) times field capacity and four (ranging from 3–5) times permanent wilting percentage, except in sandy soils. The electrical conductivities of the soil solutions at these two important soil moisture levels are greater than EC_e roughly by the same factors, except in gypsiferous soils. The conductivity of aqueous extracts (EC), including the saturation extract, can be related to that of soil solution (EC_{sw}) at known or given gravimetric soil water contents (wf) using Eq. [2].

$$EC_{sw} = \alpha(w/wf)EC \quad [2]$$

where w is the gravimetric soil water content at extraction, and α the correction factor. The value for α depends on ion composition, soil bulk density (see p. 304) and, to a lesser extent, the concentration of dissolved salts, and usually ranges from 0.7 to 1.0 (dS/m). The error in estimating EC_{sw} increases with increasing w/wf and with the increasing content in the soil of the less-soluble salt species. In general, the error becomes unacceptably high when the extraction is made at 1:1 or at higher water content, unless α is determined either empirically or theoretically (e.g., McNeal et al., 1970).

D. Determination of Sodicity: Sodium Adsorption Ratio of Saturation Extract

Since the determination of ESP requires several cumbersome procedures subject to numerous errors (Thomas, 1982), soil sodicity hazard is now commonly defined and evaluated in terms of the SAR_e . The ESP and SAR_e are quantitatively related (Rhoades, 1982b; Jurinak et al., 1984); they are nearly the same in value over the range 0 to 30 (U.S. Salinity Laboratory Staff, 1954).

Determine Ca, Mg, and Na using an atomic absorption spectrometer (or by other suitable methods such as described in *Methods of Soil Analysis*, Part 1. 2nd ed. Agronomy 9, Am. Soc. of Agron.). If large numbers of samples are to be routinely analyzed, it is extremely helpful to have this unit equipped for automatic sample transport, sequencing, siphoning, reading, and recording.

1. Apparatus

- a. Atomic absorption spectrometer.
- b. Sampling and sequencing system.
- c. Acetylene gas (C_2H_2), commercial grade.
- d. Volumetric flasks and sample vials.

2. Reagents

- a. Suppressant solution for Ca and Mg: Add 29.0 g of La_2O_3 , 250 mL of concentrated hydrochloric acid (HCl), and enough distilled water

to make up to 500-mL volume. Add a sufficient amount of this solution to the aliquot and diluent (distilled water) to achieve 10% (by volume) of this LaCl_3 solution in the final solution.

- b. Suppressant solution for Na: Add 6.358 g of LiCl and make to 1 L in distilled water (0.15 N). Add enough of this solution to the aliquot and diluent (distilled water) to give 10% (by volume) of this LiCl solution in the final solution.
- c. Standard cation solutions: Ca (0–0.4 mmol_c/L), Mg (0–0.1 mmol_c/L), and Na (0–1.0 mmol_c/L).

3. Procedure

Adjust the atomic absorption spectrometer controls and settings for each cation as recommended by the manufacturer. Set the atomic absorption spectrometer readout to read the upper and lower standard solutions. Then initiate the transport/readout system, which automatically positions a sequence of samples, siphons and aspirates the samples in the air-acetylene flame, and reads and records (as a digital printout) the concentration of the cation in the aspirated solution. Standard solutions are analyzed every 20 samples to ensure stability of instrument calibration during the automated run. Two-hundred samples can be processed per hour without attendance after the automatic sampling process is initiated. Alternatively, the same sequence of operations can be performed by hand.

4. Calculations

Concentrations of cations in the saturation extract in mmol_c/L = (atomic absorption spectrometer readout, mmol_c/L , of aspirated sample) \times (analytical dilution factor). The dilution factor must include the 1:1 predilution made at sampling time to prevent CaCO_3 precipitation during storage, if appropriate.

The SAR is calculated as

$$\text{SAR} = \text{Na} / \sqrt{(\text{Ca} + \text{Mg})/2} \quad [3]$$

where the total cation concentrations in the saturation extract are in mmol_c/L .

5. Comments

The SAR of an extract decreases with increasing soil water content at extraction due to dilution effects as well as dissolution of Ca-bearing soil minerals such as calcite and gypsum. Thus, the SAR determined in the extracts of low dilution such as the saturation extract is generally more reliable than those determined in the extracts of higher dilution. When there is no mineral dissolution, the SAR decreases in proportion to the square root of the dilution factor. The decrease in SAR in soil systems is less than this estimate, because the exchange reaction buffers the change (e.g., Oster & McNeal, 1971).

The ESP of typical soils is approximately equal to SAR_e at values below about 30. However, the ESP of gypsiferous soils is usually greater than SAR_e , partly because the measured soluble Ca and Mg concentrations include Ca- and Mg-sulfate ion pairs having no net electrical charge (e.g., Rao et al., 1968). In gypsiferous soils, Ca-sulfate ion pairs can constitute up to about one-third of the total dissolved Ca. When SO_4 concentrations are known, the SAR_e can be corrected numerically for the formation of ion pairs to yield a better estimate of ESP (Sposito & Mattigod, 1979; Oster & Sposito, 1980); however, this is seldom done routinely.

For more detailed testing needs, it is sometimes desirable to determine the compositional makeup of the other solutes in the saturation extract.

Alkalinity ($CO_3 + HCO_3$), EC, and pH determinations should be made immediately on fresh extracts or on the solutions treated with hexameta-phosphate. The cations can be determined in any sequence. The preferred sequence of anion determinations, to minimize $CaCO_3$ precipitation problems and estimate aliquot size for the more time-consuming and difficult-to-analyze anions, especially SO_4 , is alkalinity, then Cl, NO_3 , and SO_4 . Finally, B is determined. Boron is of negligible concentration compared to the major cations and anions, but it is toxic to many plants, even in small concentrations.

There are many satisfactory analytical methods for determining individual solute concentrations in extracts. Methods in common use in laboratories having modern, but not fully automated, instrumentation are described in Rhoades (1982a). Methodology more suited to laboratories without such conveniences are described in Bower and Wilcox (1965).

II. INSTRUMENTAL FIELD METHODS OF SALINITY APPRAISAL

A. Saturation Paste Conductivity

1. Principles

The EC_e may be estimated from measurement of the electrical conductivity of the saturated soil-paste (EC_p) and estimates of saturation percentage. The measurement of EC_p and the estimate of SP are made using an EC-cup of known geometry and volume. The method is suitable for both laboratory and field applications, especially the latter, because the apparatus is inexpensive, simple, and rugged and because the determination of EC_p can be made much more quickly than EC_e .

Rhoades et al. (1989b) have shown that the following relation describes the electrical conductivity of saturated soil pastes,

$$EC_p = \left[\frac{(\theta_s + \theta_{ws})^2 EC_e EC_s}{(\theta_s) EC_e + (\theta_{ws}) EC_s} \right] + (\theta_w - \theta_{ws}) EC_e \quad [4]$$

where EC_p and EC_e are as defined previously, θ_w and θ_s are the volume fractions of total water and solids in the paste, respectively, θ_{ws} is the volume fraction of water in the paste that is coupled with the solid phase to provide an electrical pathway through the paste (a series coupled pathway), and EC_s is the average specific electrical conductivity of the solid particles. The difference $(\theta_w - \theta_{ws})$ is θ_{wc} , which is the volume fraction of water in the paste that provides a continuous pathway for electrical current flow through the paste (a parallel pathway to θ_{ws}). Assuming the average particle density (ρ_s) of mineral soils to be 2.65 g/cm^3 and the density of saturation soil-paste extracts (ρ_w) to be 1.00, θ_s and θ_w are directly related to SP as follows:

$$\theta_w = SP / \left[\frac{100}{\rho_w \rho_s} + SP \right] \quad [5]$$

$$\theta_s = 1 - \theta_w. \quad [6]$$

As shown by Rhoades et al. (1989b, c), saturation percentage of mineral soils, generally, can be adequately estimated in the field for purposes of salinity appraisal from the weight of the paste-filled cup. Figure 12-1 may be used for this purpose; for details of the relations inherent in this figure see Wilcox (1951).

The EC_e can be determined for any soil solely from measurement of EC_p and SP (using Eq. [4]–[6]), if values of ρ_s , θ_{ws} , and EC_s are known. These parameters can be adequately estimated, as demonstrated by Rhoades et al. (1989b, d), for typical arid land soils of the southwestern USA. ρ_s may be assumed to be 2.65 g/cm^3 . EC_s may be estimated from SP as: $EC_s = 0.019 (\text{SP}) - 0.434$. The difference $(\theta_w - \theta_{ws})$ may be estimated from SP as: $(\theta_w - \theta_{ws}) = 0.0237 (\text{SP})^{0.6657}$.

2. Apparatus

For this determination, use any suitable conductivity meter and cup-type conductivity cell.

- Conductivity meter, temperature-compensating type.
- Conductivity cell of 50 cm^3 volume, such as the "Bureau of Soils" cup (U.S. Salinity Laboratory, 1954).
- Portable balance capable of weighing accurately to the nearest 1 g.

3. Reagents

- Standard KCl solutions, 0.010 and 0.100 *N* solution: For 0.010 *N* solution (1.412 dS/m at 25°C), dissolve 0.7456 g of KCl in distilled water, and add water to make 1 L at 25°C . For 0.100 *N* solution (12.900 dS/m at 25°C), use 7.456 g of KCl.

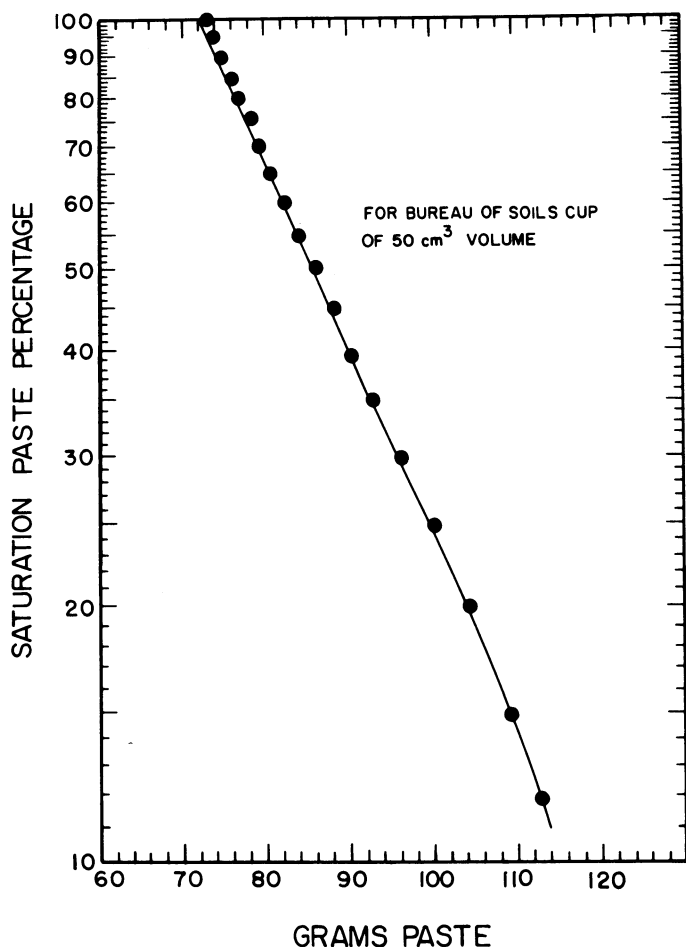


Fig. 12-1. Theoretical relation between saturation percentage (SP) and weight (in grams) of 50 cm^3 of saturated soil paste, assuming a particle density of 2.65 g/cm^3 .

4. Procedure

Rinse and fill the conductivity cup with standard KCl solution. Adjust the conductivity meter to read the standard conductivity. Rinse and fill the cup with the saturated soil-paste; tap the cup to dislodge any air entrapped within the paste. Level off the paste with the surface of the cup. Weigh the cup plus paste; subtract the cup tare weight to determine the grams of paste occupying the cup. Obtain the SP value from Fig. 12-1 corresponding to this weight. Connect the cup electrodes to the conductivity meter and determine the EC_p , corrected to 25°C , directly from the meter display. Obtain EC_e from Fig. 12-2 from EC_p using the curve corresponding to the SP value.

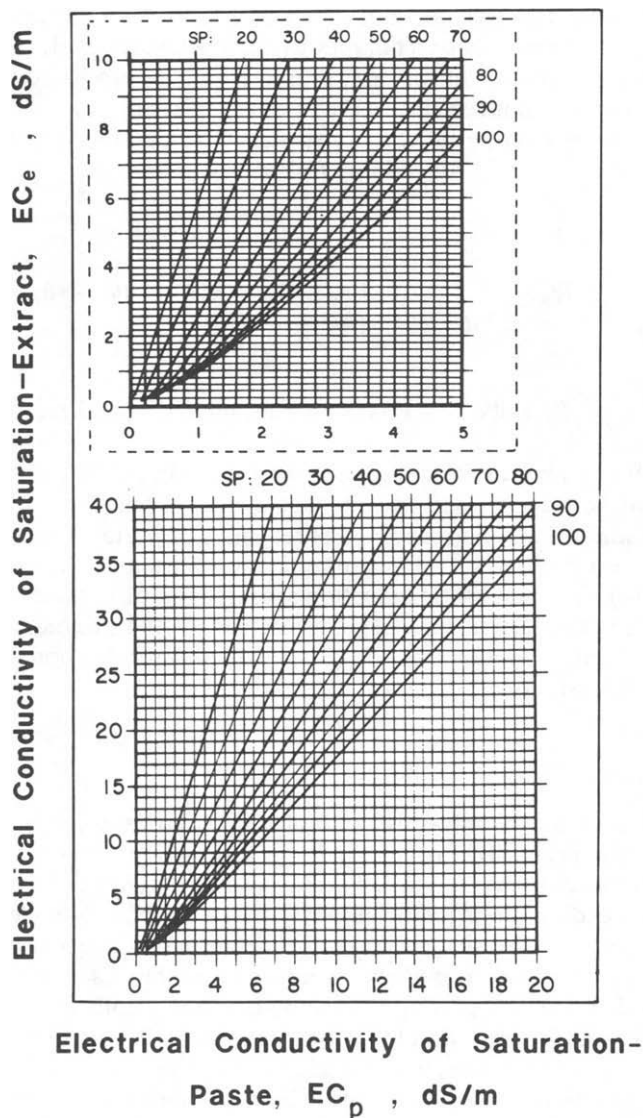


Fig. 12-2. Relations between electrical conductivity of saturated soil-paste (EC_p), electrical conductivity of saturation extract (EC_e), and saturation percentage (SP), for representative arid-land soils.

5. Comments

Sensitivity analyses and tests have shown that the estimates used in this method are generally adequate for salinity appraisal purposes of typical mineral arid-land soils of the southwestern USA. For organic soils or soils of different mineralogy or magnetic properties, these estimates may be inappropriate.

For such soils, appropriate values for ρ_s , EC_s , and θ_{ws} will need to be determined using analogous techniques to those Rhoades et al. (1989b) used. The accuracy requirements of these estimates may be evaluated using the relations given in Rhoades et al. (1989d).

The curves relating EC_p , EC_e , and SP were developed by solving Eq. [4] using the quadratic formula as follows:

$$EC_e = (-b \pm \sqrt{b^2 - 4ac})/2a \quad [7]$$

where $a = [\theta_s (\theta_w - \theta_{ws})]$, $b = [(\theta_s + \theta_{ws})^2 (EC_s) + (\theta_w - \theta_{ws})(\theta_{ws} EC_s) - (\theta_s) EC_p]$ and $c = -(\theta_{ws})(EC_s)(EC_p)$.

B. Bulk Soil Electrical Conductivity Sensors

In situ or remote devices capable of measuring electrical conductivity of the bulk soil can be used advantageously for purposes of soil salinity appraisal, monitoring, and mapping. Three kinds of portable sensors are now available, each with its own advantages and limitations: (i) four-electrode sensors, (ii) electromagnetic induction sensors, and (iii) time domain reflectometry (TDR) insertion parallel guide electrodes. All three measure the electrical conductivity of the bulk soil (EC_a), which depends upon its soil water content and salt concentration.

1. Principles

Because most soil minerals are insulators, electrical conduction in moist, saline soils is primarily through the large water-filled pores, which contain the dissolved salts (electrolytes). There is also a relatively small contribution of exchangeable cations (associated with the solid phase) to electrical conduction in soils, the so-called surface conduction (EC_s), because these electrolytes are more limited in their amounts and mobilities. The value of EC_s is assumed, for practical purposes, to be essentially constant for any given saline soil. EC_s is coupled in series with the electrolyte present in the water films associated with the solid surfaces and in the small water-filled pores that bridge adjacent particles to provide a secondary pathway for current flow in moist soils. This pathway acts in parallel with the major, continuous flow pathway (large water-filled pores). The relative flow of current in the two pathways depends on the solute concentration of the soil water, the magnitude of EC_s , and the contents of water in the two different categories of pores.

A mathematical description of the above model of electrical current flow in soils is given in Eq. [8] after Rhoades et al. (1989c):

$$EC_a = \left[\frac{(\theta_s + \theta_{ws})^2 EC_{ws} EC_s}{(\theta_s) EC_{ws} + (\theta_{ws}) EC_s} \right] + (\theta_w - \theta_{ws}) EC_{wc} \quad [8]$$

where EC_a , θ_s , θ_w , and EC_s are as previously defined, θ_{ws} and $(\theta_w - \theta_{ws})$ are the volumetric soil water contents in the series-coupled pathway (the fine water-filled pores) and the separate continuous liquid pathway (large water-filled pores), respectively, and EC_{ws} and EC_{wc} are the specific electrical conductivities of the soil water that is in the two corresponding pathways, respectively.

The relation between EC_{ws} , EC_{wc} , and EC_e is (after Rhoades et al., 1989c):

$$(EC_{wc} \theta_{wc} + EC_{ws} \theta_{ws})/\rho_b = EC_e SP/100$$

where ρ_b is the bulk density of the soil. For practical purposes of salinity appraisal, it is assumed that $EC_{wc} \approx EC_{ws}$ and, therefore, that $(EC_w \theta_w) \approx (EC_{wc} \theta_{wc} + EC_{ws} \theta_{ws})$. Data exist to support the general validity of this assumption for typical field soils (Rhoades et al., 1989d).

The other relations used in the practical application of EC_a measurements to appraise soil salinity are (after Rhoades et al., 1990):

$$SP = 0.76 (\%C) + 27.25, \quad [10]$$

$$\rho_b = 1.73 - 0.0067 (SP), \quad [11]$$

$$\theta_s = \rho_b/2.65, \quad [12]$$

$$\theta_{wfc} = SP \cdot \rho_b/200, \quad [13]$$

$$\theta_w = \theta_{wfc} \cdot FC/100, \quad [14]$$

$$\theta_{ws} = 0.639 \theta_w + 0.011, \text{ and} \quad [15]$$

$$EC_s = 0.019 SP - 0.434 \quad [16]$$

where $\%C$ is clay percentage as estimated by "feel" methods, θ_{wfc} is the estimated volumetric water content at field capacity, and FC is the percent water content of the soil relative to that at field capacity, as estimated by the feel method. Use of the above relations permits the EC_e to be estimated in the field sufficiently accurately for salinity appraisal purposes from the measurement of EC_a and the estimates of $\%C$ and θ_{wfc} made by feel methods. That such procedures are generally adequate for typical arid land mineral soils of the southwestern USA has been demonstrated by Rhoades et al. (1990).

2. Apparatus

a. Four-Electrode Sensors

A combination electric current source and resistance meter, four metal electrodes, and connecting wire are needed for large soil volume (surface ar-

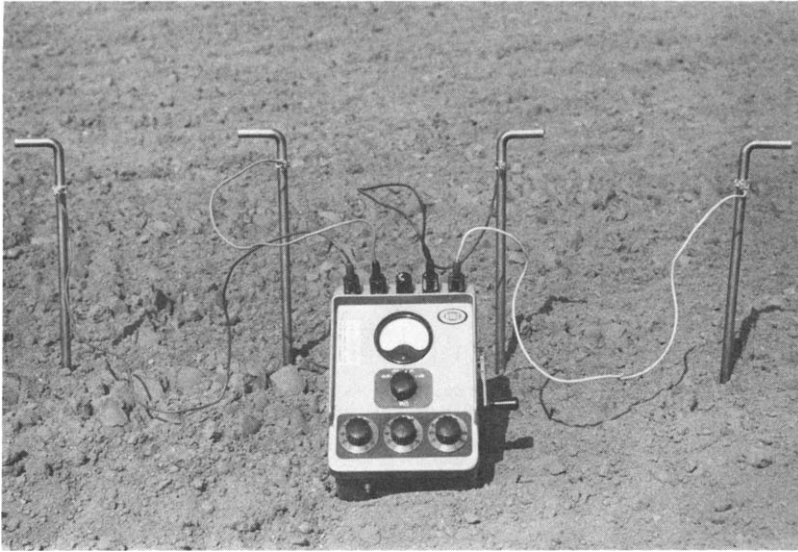


Fig. 12-3. Photograph of four electrodes positioned in a surface array and a combination electric generator and resistance-meter.

ray) measurements (Fig. 12-3). A four-electrode salinity probe, in which the electrodes are built into the probe [(Rhoades & van Schilfgaarde, 1976)] is needed for small soil volume measurements (Fig. 12-4). The current source-meter unit may be either a hand-cranked generator (Fig. 12-3) or a battery-powered type (Fig. 12-4). Units designed for geophysical purposes generally read in ohms and should measure from 0.1 to 1000 ohms for general soil

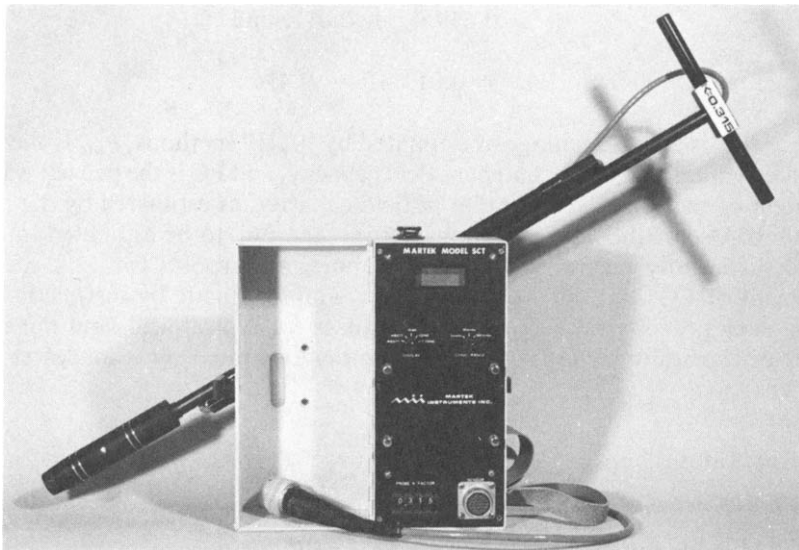


Fig. 12-4. Photograph of commercial four-electrode conductivity probe and generator-meter.

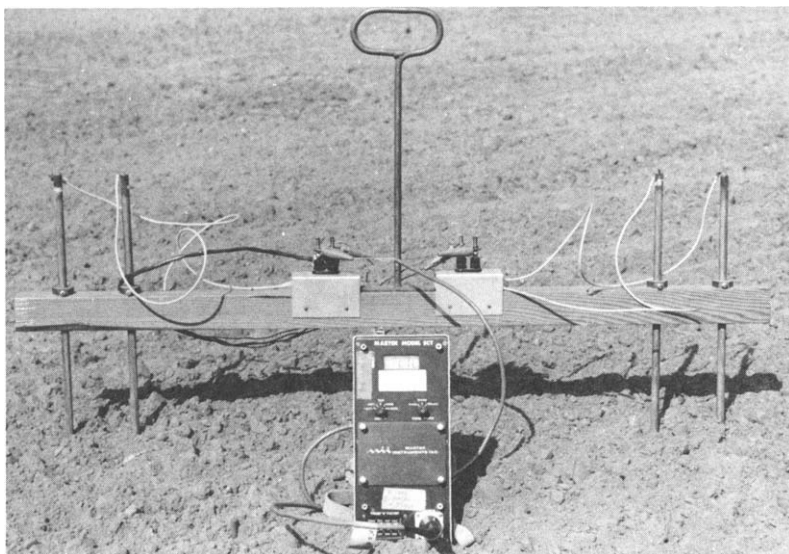


Fig. 12-5. Photograph of a “fixed-array” four-electrode apparatus and commercial generator-meter.

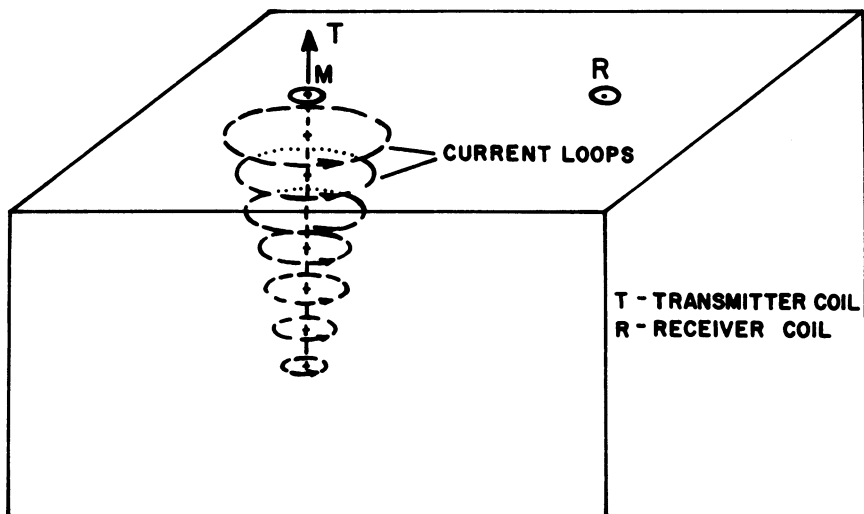
salinity measurement needs. Units specifically designed for use with the four-electrode salinity probe are much smaller and more convenient (Austin & Rhoades, 1979). A commercial unit, Martek SCT², reads directly in EC_a corrected to 25 °C (Fig. 12-4).

Electrodes are made of stainless steel, copper, brass, or almost any other corrosion-resistant metal. Array electrode size is not critical, except that the electrode must be small enough to be easily inserted into the soil, to not tip over and maintain firm contact with the soil, when inserted to a depth of 5 cm or less. Electrodes 1.0 to 1.25 cm in diameter by 45 cm long are convenient for most array purposes, although smaller electrodes are preferred for determination of EC_a within shallow depths (< 30 cm). Any flexible, well-insulated, multi-stranded, 12- to 18-gauge wire is suitable for connecting the array electrodes to the meter.

For survey or traverse work, the array electrodes may be mounted in a board with a handle (see Fig. 12-5) so that soil-resistance measurements can be made quickly for a given inter-electrode spacing (Rhoades & Halvorson, 1977). These “fixed-array” units save the time involved in positioning the electrodes. For most purposes, an inter-electrode spacing of 30 or 60 cm is adequate and convenient (wider spacings require lengthy, cumbersome units).

b. Electromagnetic Induction Sensors

The basic principle of operation of the EM soil electrical conductivity meter is shown schematically in Fig. 12-6. A transmitter coil located in one end of the instrument induces circular eddy current loops in the soil. The



INDUCED CURRENT FLOW IN GROUND

Fig. 12-6. Diagram showing the principle of operation of electromagnetic induction soil conductivity sensor.

magnitude of these loops is directly proportional to the conductivity of the soil in the vicinity of that loop. Each current loop generates a secondary electromagnetic field that is proportional to the value of the current flowing within the loop. A fraction of the induced electromagnetic field from each loop is intercepted by the receiver coil and the sum of these signals is amplified and formed into an output voltage that is linearly related to a depth-weighted soil EC_a .

Figure 12-7 shows the commercially available EM soil salinity sensor (Geonics EM-38²) being held in the vertical and horizontal (coils) positions. This device has an inter-coil spacing of 1 m, operates at a frequency of 13.2 kHz, is powered by a 9-V battery, and reads *depth-weighted* EC_a directly. The coil configuration and inter-coil spacing were chosen to permit measurement to effective depths of approximately 1 and 2 m when placed at ground level in a horizontal and vertical configuration, respectively. The device contains appropriate circuitry to minimize instrument response to the magnetic susceptibility of the soil and maximize response to EC_a .

c. Time Domain Reflectometry Sensors

With the use of TDR sensors, the apparent dielectric constant of the soil, ϵ , is obtained by measuring the transit time, t , of a voltage pulse applied to the parallel transmission line (dual-rod sensor) of length L embedded in the soil of electrical conductivity EC_a , and applying the relation:

$$\epsilon = (ct/2L)^2 \quad [17]$$

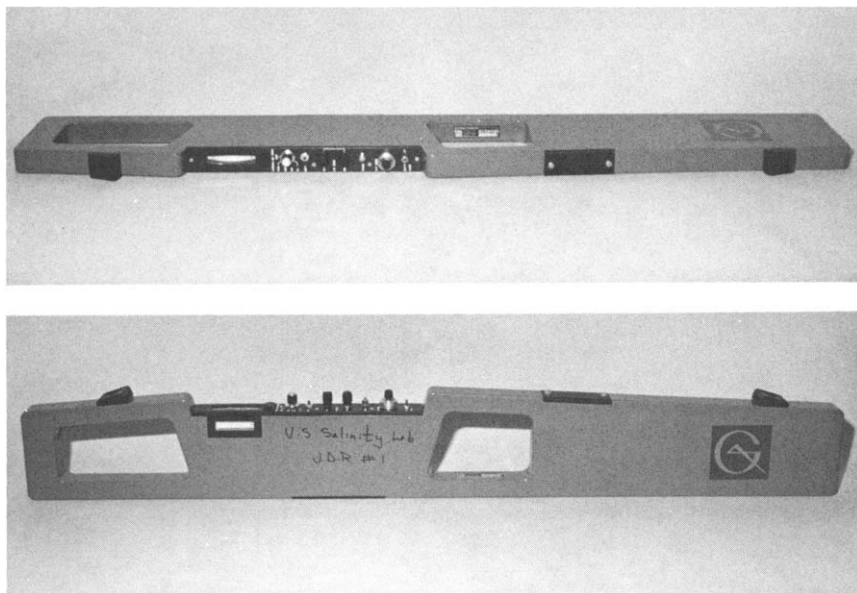


Fig. 12-7. Photograph of electromagnetic induction soil conductivity sensor.

where c is the velocity of light in vacuum. The signal is attenuated in proportion to EC_a so that the transmitted voltage, V_T , is reduced to V_R according to:

$$V_R = V_T \exp(-2\alpha L). \quad [18]$$

The attenuation coefficient, α , increases linearly with EC_a as:

$$\alpha = 60\pi EC_a / (\epsilon)^{1/2}. \quad [19]$$

Figure 12-8 shows a TDR-insertion sensor (homemade unit) and a commercially available TDR tester (Tektronix 7603 oscilloscope-7512 TDR sampler²).

Recent laboratory studies using this equipment have shown that EC_a and EC_w are well correlated with V_R/V_T (Dalton et al., 1984). The TDR method offers the distinct advantage of measuring both water content and soil electrical conductivity simultaneously; however, the practical attributes of this method have not yet been fully evaluated.

²Mention of trademark or proprietary products in this manuscript does not constitute a guarantee or warranty of the product by the USDA or by the Texas Agric. Exp. Stn., and does not imply its approval to the exclusion of other products that may also be suitable.

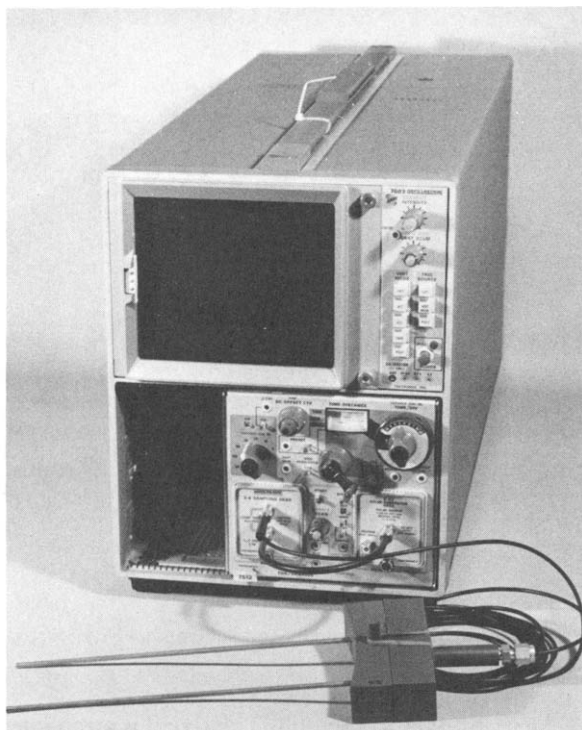


Fig. 12-8. Photograph of time domain reflectometry (TDR) probe and meter.

3. Procedures

a. Large Volume Measurements

For the purpose of determining soil salinity of entire root zones, or some fraction thereof, it is desirable to make the measurement when the current flow is concentrated within this soil depth. This is accomplished with the four-electrode equipment by selecting the appropriate spacing between the two current (outer) electrodes that are inserted into the soil surface to a depth of about 5 cm. In this arrangement, four electrodes are placed in a straight line. With conventional geophysical resistivity measurements the electrodes are equally spaced in the so-called *Wenner array* (Rhoades & Ingvalson, 1971). With the Martek SCT meter, each of the inner pair of electrodes is placed inward from its closest outer-pair counterpart, a distance equal to 10% of the spacing between the outer pair. The inner pair is used to measure the potential while current is passed between the outer pair. The effective depth of current penetration for either configuration (in the absence of appreciable soil layering) is equal to about one-third the outer-electrode spacing, y , and the average soil salinity is measured to approximately this depth (Rhoades & Ingvalson, 1971; Halvorson & Rhoades, 1976). Thus, by varying the spacing between current electrodes, one can measure average soil salinity to different depths and within different volumes of soil. Another advantage of this

method is the relatively large volume of soil measured as compared with soil samples. The volume of measurement is about $(\pi y/3)^3$. Hence, effects of small-scale variations in field-soil salinity on sampling requirements can be minimized by these large-volume measurements.

For measurements taken in the Wenner array (electrodes equally spaced) using geophysical-type meters that measure resistance, the soil electrical conductivity is calculated, in dS/m, from:

$$EC_a = 159.2 f_t / a R_t \quad [20]$$

where a is the distance between the electrodes in cm, R_t is the measured resistance in ohms at the field temperature t , and f_t is a factor³ to adjust the reading to a reference temperature of 25 °C. For measurements made with the Martek SCT meter, a factor is supplied in chart form for each spacing of outer electrodes; this factor is dialed into the meter and the correct soil EC_a reading is displayed in the meter readout.

Large volumes of soil can also be measured with the electromagnetic induction technique. The volume and depth of measurement can be increased by increasing the spacing between coils, reducing the current frequency, and positioning the coils so that their axis is vertical to the soil surface plane. The effective depths of measurement of the Geonics EM-38 device are about 1 and 2 m when it is placed on the ground and the coils are positioned horizontally and vertically, respectively. The EM-38 device does not integrate soil EC_a linearly with depth. The 0 to 0.30, 0.30 to 0.61, 0.61 to 0.91, and 0.91 to 1.22 m depth intervals contribute about 43, 21, 10, and 6%, respectively, to the EC_a reading of the EM unit when positioned on homogeneous ground in the horizontal position (Rhoades & Corwin, 1981). Thus, the weighted bulk soil electrical conductivity read by the EM device in this configuration (EM_{HO}) is given by:

$$EM_{HO} = 0.43EC_{0-0.3} + 0.21EC_{0.3-0.6} + 0.10EC_{0.6-0.9} + 0.06EC_{0.9-1.2} + 0.2EC_{>1.2} \quad [21]$$

where the subscript designates the depth interval in meters.

It is desirable to determine soil EC_a by depth intervals for calculating soil salinity within various parts of the root zone as needed for making assessments and management decisions. Since the proportional contribution of each soil depth interval to EC_a , as measured by the EM unit, can be varied by raising it aboveground to higher heights, it is possible to calculate the EC_a -depth relation from a succession of EM measurements made at various heights aboveground (Rhoades & Corwin, 1981). The EC_a values of each soil-depth interval are simply correlated with the succession of EM readings (0-4) as:

³ $f_t = (0.0004)(T^2) - (0.043)(T) + 1.8149$; based on data given on p. 90 in U.S. Salinity Laboratory Staff (1954).

Table 12-1. Equations for predicting EC_a within different soil-depth increments from electromagnetic measurements made with the EM-38 device placed on the ground in the horizontal (EM_H) and vertical (EM_V) configurations.

Depth, cm	Equations for electrical conductivity†
<u>for $EM_H \leq EM_V$</u>	
0-30	$\hat{EC}_a = 3.023 \hat{EM}_H - 1.982 \hat{EM}_V$
0-60	$\hat{EC}_a = 2.757 \hat{EM}_H - 1.539 \hat{EM}_V - 0.097$
0-90	$\hat{EC}_a = 2.028 \hat{EM}_H - 0.887 \hat{EM}_V$
30-60	$\hat{EC}_a = 2.585 \hat{EM}_H - 1.213 \hat{EM}_V - 0.204$
60-90	$\hat{EC}_a = 0.958 \hat{EM}_H + 0.323 \hat{EM}_V - 0.142$
<u>for $EM_H > EM_V$</u>	
0-30	$\hat{EC}_a = 1.690 \hat{EM}_H - 0.591 \hat{EM}_V$
0-60	$\hat{EC}_a = 1.209 \hat{EM}_H - 0.089$
0-90	$\hat{EC}_a = 1.107 \hat{EM}_H$
30-60	$\hat{EC}_a = 0.554 \hat{EM}_H + 0.595 \hat{EM}_V$
60-90	$\hat{EC}_a = -0.126 \hat{EM}_H + 1.283 \hat{EM}_V - 0.097$

† \hat{EC}_a , \hat{EM}_H , and \hat{EM}_V are the fourth roots of EC_a , EM_H , and EM_V .

$$EC_{a, 0-0.3} = \beta_0 EM_0 + \beta_1 EM_1 + \beta_2 EM_2 + \beta_3 EM_3 + \beta_4 EM_4 \quad [22a]$$

$$EC_{a, 0.3-0.6} = \gamma_0 EM_0 + \gamma_1 EM_1 + \gamma_2 EM_2 + \gamma_3 EM_3 + \gamma_4 EM_4. \quad [22b]$$

The values of the coefficients of Eq. [22] reported by Rhoades and Corwin (1981) are generally applicable, though exceptions have been found.

Another series of equations and coefficients have been derived to obtain EC_a within soil-depth intervals from just two measurements made with the magnetic coils of the EM instrument positioned at ground level, first horizontally and then vertically (Corwin & Rhoades, 1982; Rhoades et al., 1989a). For the depth increment x_1 to x_2 , the equations are of the form:

$$EC_{a, x_1-x_2} = k_H EM_H - k_V EM_V + k \quad [23]$$

where EM_V and EM_H are the apparent bulk soil electrical conductivities measured electromagnetically at the soil surface in the vertical and horizontal positions, respectively; x_1 - x_2 is the soil-depth increment in centimeters and k_H , k_V , and k are empirically determined coefficients for the depth increment. Equation [23] is more easily solved than Eq. [22] and is almost as accurate. Values of the coefficients are given in Table 12-1, after Rhoades et al. (1989a).

b. Small Volume Measurements

Sometimes information on salinity distribution within a localized volume of the whole root zone is desired, such as that within the seed bed or under

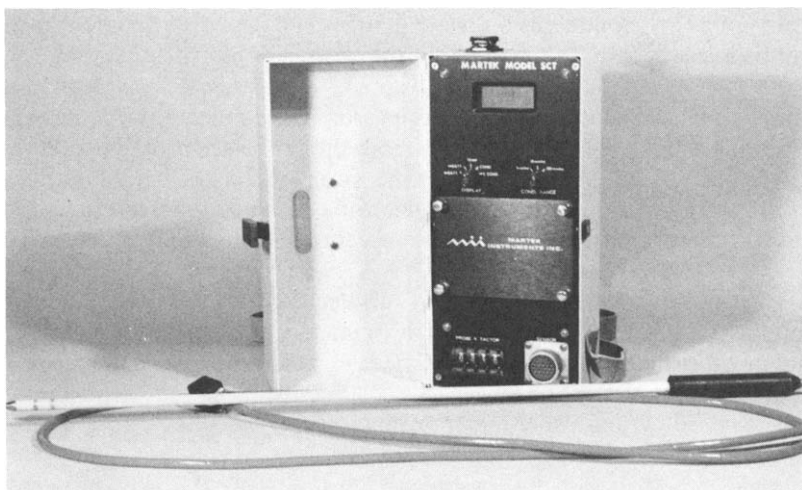


Fig. 12-9. Photograph of commercial seed-bed four electrode conductivity probe and generator-meter.

the furrows. For such conditions, the four-electrode salinity probe (Rhoades & van Schilfgaarde, 1976) and burial-type probe (Rhoades, 1979) are recommended. The seed bed probe (see Fig. 12-9) is designed to be directly inserted into the soil. In the larger probes (see Fig. 12-4 and 12-10), four



Fig. 12-10. Photograph of burial-type four electrode conductivity probe and generator-meter.

annular rings are molded in a plastic matrix that is slightly tapered so that it can be inserted into a hole made to the desired depth with a coring tube. In the portable version (Fig. 12-4), the probe is attached to a shaft (handle) through which the electrical leads are passed and connected to a meter. In the burial unit (Fig. 12-10), the leads from the probe are brought to the soil surface. The volume of sample under measurement can be varied by changing the spacing between the current electrodes. The commercial unit, Martek SCT², has a spacing of 6.6 cm and measures a soil volume of about 2350 cm³.

To determine soil EC_a with the four-electrode probe (Fig. 12-4), core a hole in the soil to the desired depth of measurement using a Lord² soil sampling tube (or sampler of similar diameter). Insert the four-electrode probe into the soil and record the resistance, or the displayed EC_a depending on the meter used. When using meters which display resistance, EC_a in dS/m is calculated as:

$$EC_a = k f_t / R_t \quad [24]$$

where k is an empirically determined geometry constant (cell constant) for the probe in units of 1000 cm⁻¹, R_t is the resistance in ohms at the field temperature, and f_t is a factor to adjust the reading to a reference temperature of 25°C (see footnote 3).

4. Calculations

The EC_w is calculated from the solution of Eq. [8] and [10] to [16] using the quadratic formula:

$$EC_w = (-b \pm \sqrt{b^2 - 4ac})/2a \quad [25]$$

where $a = -[(\theta_s)(\theta_w - \theta_{ws})]$, $b = [(\theta_s EC_a) - (\theta_s + \theta_{ws})^2 (EC_s) - (\theta_w - \theta_{ws})(\theta_{ws} EC_s)]$, and $c = [(\theta_w)(EC_s)(EC_a)]$. Then EC_e can be solved from Eq. [19]. Alternatively obtain EC_e, given measurements of EC_a and reasonable estimates of %C and θ_w , using Fig. 12-11a-l.

5. Comments

Sensitivity analyses and tests have shown that the estimates used in this method are generally adequate for salinity appraisal purposes of typical mineral, arid-land soils of the southwestern USA (Rhoades et al., 1989a, 1990). For organic soils or soil of different mineralogy or magnetic properties, these estimates may be inappropriate. For such soils, appropriate estimating procedures will have to be developed using analogous techniques to those used by Rhoades et al. (1990). The accuracy requirements of these estimates may be evaluated using the relations given in Rhoades et al., 1989d).

As seen in Fig. 12-11a-l, water content (as well as salinity) affects soil electrical conductivity, and determinations are made preferably when the soil is near field capacity. However, measurements and salinity appraisals can

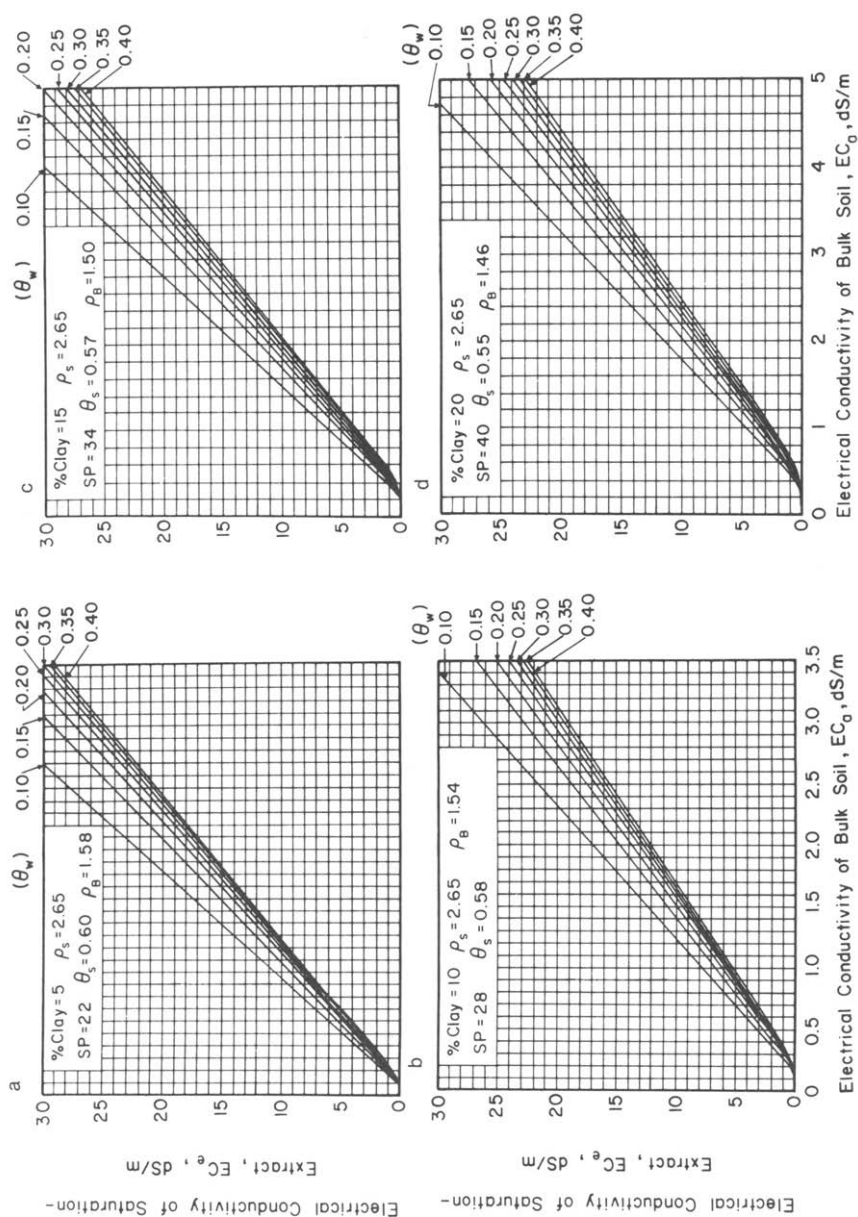


Fig. 12-11a-1. Relations between electrical conductivity of bulk soil (EC_b), electrical conductivity of saturation-extract (EC_e), soil volumetric water content (θ_w), and soil clay content (% clay), for representative arid-land soils.

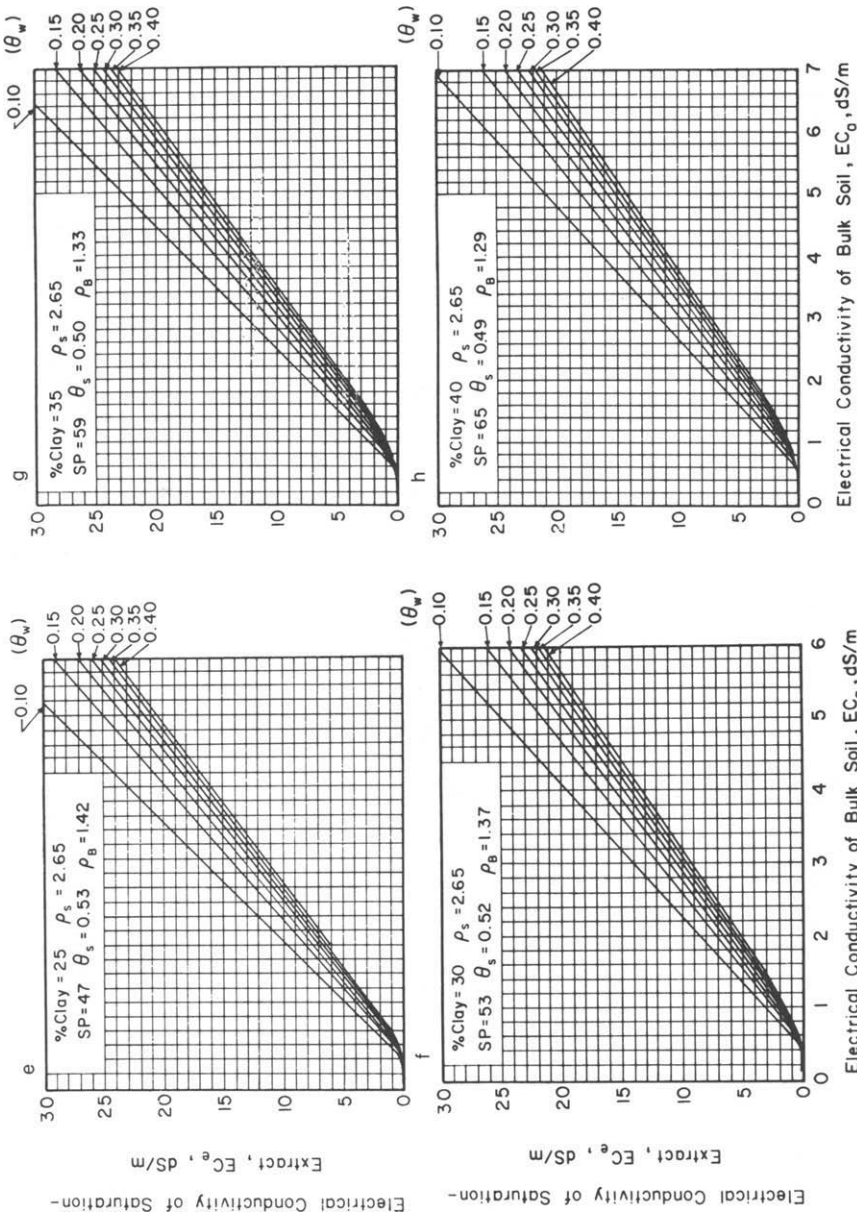


Fig. 12-11a-1. Continued.

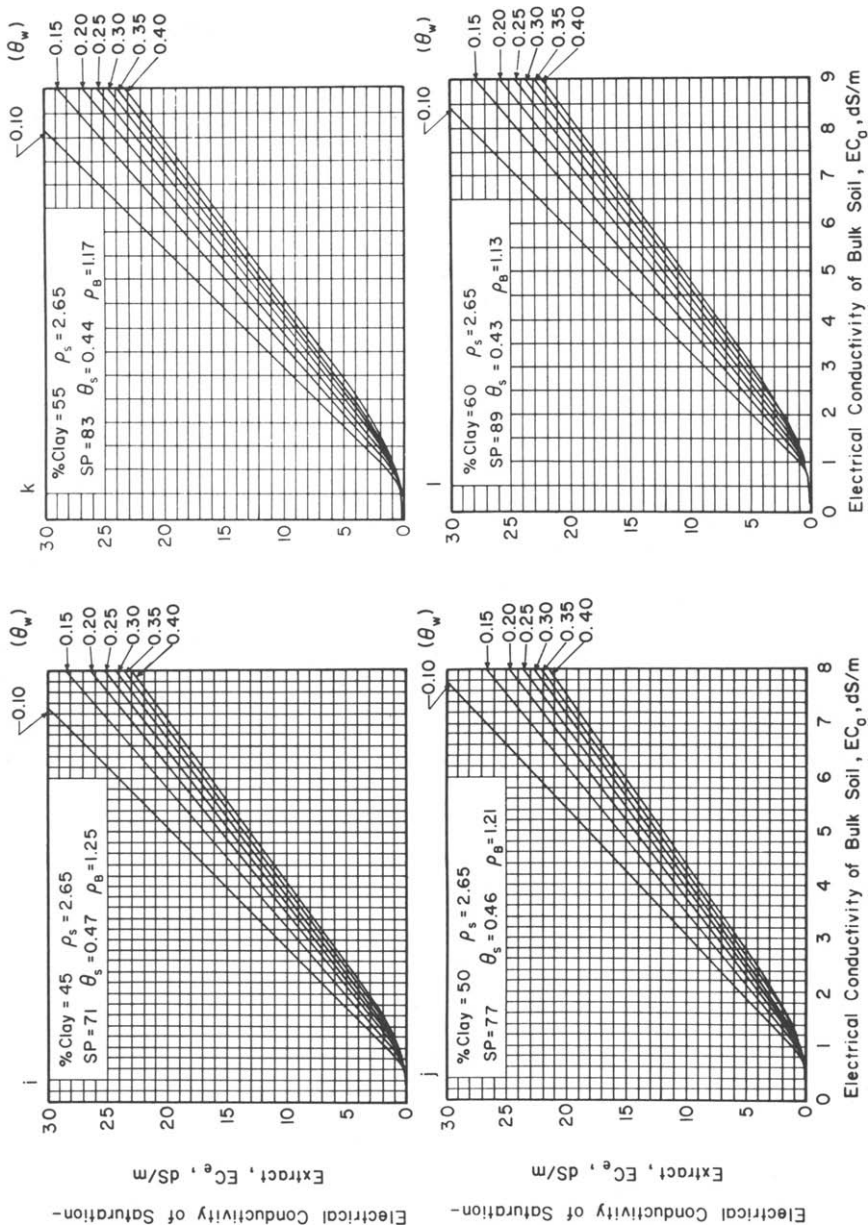


Fig. 12-11a-l. Continued.

be made at lower water contents as described above. However, a certain minimum water content is required in the soils for the measurements of EC_a and the model calculations to be valid; this water content is about 10% on a gravimetric basis, though it may be somewhat higher for very sandy soils.

The ratio $SP/100$ in Eq. [9] may be replaced by the ratio (θ_e/ρ_p) , where ρ_p is the bulk density of the saturated paste and θ_e is the total volumetric content of water in the saturated paste. It should be noted that $(EC_e \theta_e)$ is not equivalent to $(EC_w \theta_w)$ because different amounts of soil are involved in the two measurements. The relation between these two products is given in Eq. [9]. θ_e is related to SP as follows:

$$\theta_e = SP/[(\rho_e/100/\rho_s) + SP] \quad [26]$$

where ρ_e is the density of the saturation extract ($\sim 1.00 \text{ g/cm}^3$). ρ_p (soil dry weight basis) is related to SP as follows:

$$\rho_p = 100[(100/\rho_s) + (SP/\rho_e)]. \quad [27]$$

These relations are described in more detail elsewhere (Rhoades et al., 1989b, 1990).

If devices are available to measure θ_w , or if other more appropriate values for any of the other estimated parameters are available, then, of course, they should be used in place of the estimates obtained by the methods given here. If more accurate measurements of EC_e or EC_w are required than can be obtained by the estimation procedures provided, quantitative measurements of θ_w , EC_s , and ρ_b , should be made using appropriate methods.

The depth-weighted value of EC_e , as calculated from the value of EM_{HO} measured by the EM-38 unit (see Eq. [21]), may be appropriate to use as a single index of soil salinity in some cases, as it roughly corresponds to the water-extraction behavior of plants. Irrigated crops tend to remove the soil approximately in the proportions 40:30:20:10 by successively deeper quarter-fractions of their root zone, which is about 1 m in depth for many crops, and to respond to water uptake-weighted salinity (Bernstein & Francois, 1973; Rhoades & Merrill, 1976).

III. DIAGNOSIS GUIDELINES

A. Salinity Hazard

Excess salinity (essentially independent of its composition) in the root zone adversely affects the growth of established plants by a general reduction in growth rate. Salt increases the energy that must be expended by the plant to extract water from the soil and to make the biochemical adjustments necessary to grow under stress (Maas, 1984, 1985). This energy is diverted from the processes that lead to normal growth and yield. Hence, the potential adverse effects of salinity on crop production should be assessed using

information of salinity levels in the regions of the soil where the roots are actively extracting water. A problem is likely if the level of salinity in the vicinity of the active rootlets exceeds the tolerances of the crops for growth and yield.

To assess the likelihood of a salinity problem for conventionally irrigated and established crops, first estimate the depth-average salinity of the major root zone (i.e., where the majority of water extraction occurs). When high frequency or drip irrigation is used, estimate the water-uptake-weighted mean by using an appropriate soil water extraction pattern. Secondly, determine the mean and the extremes of salinity over the area of concern. If there are sufficient number of measurements (at least 10), compute the standard deviation. If no salt damage is permitted in any part of the area, the maximum salinity observed in the area should be taken as the soil salinity level for the field. If salt problems are permitted to occur in about 15% of the area, the sum of mean and standard deviation (SD) should be used as the salinity level. If the SD is small (e.g., < 15% in coefficient of variability, CV), the sample mean may be used as the soil salinity level. Thirdly, compare the value of the soil salinity level obtained with that of the salt tolerance of the crop(s) to be grown. The salt tolerances of crops based on growth and yield are given in Table 12-2, after Maas and Hoffman (1977) and Maas (1985), in terms of their threshold values and percentage decreases in yield per unit increase of soil salinity above the threshold (where the unit of soil salinity is the electrical conductivity of the extract of a saturated soil paste in dS/m). Such salt-tolerance data cannot provide accurate, quantitative crop yield losses from salinity for every situation, since actual response to salinity varies with growing conditions. Such conditions include climate, irrigation method, agronomic management, and crop variety. Such salt-tolerance data are useful, however, to diagnosis the *likelihood* of salinity problems and predict how one crop might fare relative to another one under similar salinity conditions. For detailed information on the tolerance of specific crops to salinity refer to Francois and Maas (1978).

Improvement in diagnosis can be made by using computed average salinity of the soil solution per se rather than that of the saturation extract (see section II.C.4). Salinity of the saturation extract does not take into account the effect of soil water depletion on increasing salinity of the soil water between irrigations (Rhoades et al., 1981; Miyamoto et al., 1985a). With the use of high-frequency irrigation methods, the use of the saturation extract is even less appropriate as a measure of soil water salinity (Rhoades, 1982b). Soil solution-based salinity appraisal is also preferred for sandy soils, especially those irrigated with saline waters. The EC_e values of such soils are considerably less than those of medium-textured soils similarly treated (e.g., Longenecker, 1973). In fact, it is common to underrate the salt hazard of sandy soils irrigated with saline waters. The use of soil solution-based salinities necessitates the conversion of crop salt-tolerance data from EC_e to EC_{sw} (see Eq. [9]).

The salt-tolerance data of Table 12-2 apply most directly to flood-irrigated crops and typical irrigation management, they are less applicable

Table 12-2. Relative salt tolerances of agricultural crops. After Maas and Hoffman (1977).

Crop	Scientific name	Threshold	Decrease in
		salinity of saturation extract	yield at soil salinities above the threshold
		dS/m	% (dS/m)
	<u>Sensitive crops</u>		
Bean	<i>Phaseolus vulgaris</i> L.	1.0	19
Carrot	<i>Daucus carota</i> L.	1.0	14
Strawberry	<i>Fragaria</i> sp.	1.0	33
Onion	<i>Allium cepa</i> L.	1.2	16
Almond	<i>Prunus dulcis</i> (Mill.)	1.5	19
Blackberry	<i>Rubus</i> sp.	1.5	22
Boysenberry	<i>Rubus ursinus</i>	1.5	22
Plum, prune	<i>Prunus domestica</i> L.	1.5	18
Apricot	<i>Prunus armeniaca</i> L.	1.6	24
Orange	<i>Citrus sinensis</i> (L.)	1.7	16
Peach	<i>Prunus persica</i>	1.7	21
Grapefruit	<i>Citrus paradisi</i> Macfad.	1.8	16
	<u>Moderately sensitive crops</u>		
Turnip	<i>Brassica rapa</i>	0.9	9.0
Radish	<i>Raphanus sativus</i> L.	1.2	13
Lettuce	<i>Lactuca sativa</i> L.	1.3	13
Clover, berseem	<i>T. alexandrinum</i> L.	1.5	5.7
Clover, strawberry	<i>T. fragiferum</i> L.	1.5	12
Clover, red	<i>T. pratense</i> L.	1.5	12
Clover, alsike	<i>Trifolium hybridum</i> L.	1.5	12
Clover, ladino	<i>Trifolium repens</i> L.	1.5	12
Foxtail, meadow	<i>Alopecurus pratensis</i> L.	1.5	9.6
Grape	<i>Vitaceae</i>	1.5	9.6
Orchardgrass	<i>Dactylis glomerata</i> L.	1.5	6.2
Pepper	<i>Capsicum annuum</i> L.	1.5	14
Sweet potato	<i>Ipomoea batatas</i> (L.)	1.5	11
Broadbean	<i>Vicia faba</i> L.	1.6	9.6
Corn	<i>Zea mays</i> L.	1.7	12
Flax	<i>Linum usitatissimum</i> L.	1.7	12
Potato	<i>Solanum tuberosum</i> L.	1.7	12
Sugarcane	<i>Saccharum officinarum</i> L.	1.7	5.9
Cabbage	<i>B. oleracea capitata</i>	1.8	9.7
Celery	<i>Apium graveolens</i> L.	1.8	6.2
Corn (forage)	<i>Zea mays</i> L.	1.8	7.4
Alfalfa	<i>Medicago sativa</i> L.	2.0	7.3
Spinach	<i>Spinacia oleracea</i> L.	2.0	7.6
Trefoil, big	<i>Lotus uliginosus</i>	2.3	19
Cowpea (forage)	<i>Vigna unguiculata</i>	2.5	11
Cucumber	<i>Cucumis sativus</i> L.	2.5	13
Tomato	<i>Lycopersicon Lycopersicum</i>	2.5	9.9
Broccoli	<i>Brassica oleracea botrytis</i>	2.8	9.2
Vetch, common	<i>Vicia angustifolia</i>	3.0	11
Rice, paddy	<i>Oryza sativa</i> L.	3.0	12
Squash, scallop	<i>Cucurbita pepo melopepo</i>	3.2	16
	<u>Moderately tolerant crops</u>		
Wildrye, beardless	<i>E. triticoides</i> Buckl.	2.7	6.0
Sudangrass	<i>Sorghum sudanense</i>	2.8	4.3
Wheatgrass, std. crested	<i>Agropyron desertorum</i>	3.5	4.0

(continued on next page)

Table 12-2. Continued.

Crop	Scientific name	Threshold salinity of saturation extract	Decrease in yield at soil salinities above the threshold
		dS/m	% (dS/m)
	Moderately sensitive crops		
Fescue, tall	<i>Festuca elatior</i>	3.9	5.3
Beet, red	<i>Beta vulgaris</i> L.	4.0	9.0
Hardinggrass	<i>Phalaris tuberosa</i>	4.6	7.6
Squash, zucchini	<i>C. pepo melopepo</i>	4.7	9.4
Cowpea	<i>Vigna unguiculata</i> (L.)	4.9	12
Soybean	<i>Glycine max</i> (L.)	5.0	20
Trefoil, birdsfoot	<i>Lotus corniculatus</i> L.	5.0	10
Ryegrass, perennial	<i>L. perenne</i> L.	5.6	7.6
Wheat, durum	<i>T. durum</i> Desf.	5.7	5.4
Barley (forage)	<i>Hordeum vulgare</i> L.	6.0	7.1
Wheat	<i>Triticum aestivum</i> L.	6.0	7.1
Sorghum	<i>Sorghum bicolor</i> (L.)	6.8	16
	Tolerant crops		
Date palm	<i>Phoenix dactylifera</i> L.	4.0	3.6
Bermudagrass	<i>Cynodon dactylon</i> (L.)	6.9	6.4
Sugarbeet	<i>Beta vulgaris</i> L.	7.0	5.9
Wheatgrass, fairway crested	<i>A. cristatum</i>	7.5	6.9
Wheatgrass, tall	<i>A. elongatum</i>	7.5	4.2
Cotton	<i>Gossypium hirsutum</i> L.	7.7	5.2
Barley	<i>Hordeum vulgare</i> L.	8.0	5.0

to high-frequency forms of irrigation, such as drip irrigation. Sprinkler-irrigated crops may suffer additional damage from foliar salt uptake and "burn" caused by contact with the spray. The available data-base for predicting yield losses from foliar spray effects is limited (Maas, 1984, 1985). The degree of foliar injury depends not only upon salinity of the irrigation water but also upon weather conditions, the size of sprinkler droplets, crop type, and growth stage. The tolerances of crops to foliar-induced salt damages does not usually coincide with that of root-induced damage. In the case of sprinkler irrigation, it is necessary to evaluate irrigation water salinity in addition to soil salinity.

Salinity also adversely affects crop establishment, especially when furrow-irrigation is used. In fact, obtaining a good crop stand is among the hardest tasks associated with crop production in saline areas. Once the crop is established, management risks are substantially reduced. The reason for the high risk at the seedling establishment stage is partly related to the lower salt tolerance of seedlings compared to established plants. However, the major reason for salt damage to seedlings is the exposure to pronounced salt accumulation occurring at or near the soil surface in the immediate vicinity of the seed or small plant. The salinity of the soil solution at the near-surface of furrow irrigated beds can easily reach that of sea water in a matter of several weeks (e.g., Miyamoto et al., 1985b). Salt concentrations in crop beds

vary markedly with depth and time. Therefore, it is essential to have a clear specification of the depth and time of sampling when interpreting such salinity data.

Suppose that soil samples were collected at seedling depths (excluding the surface salt crust) immediately before or after time of seeding. The salinity readings can then be used to assess potential effects on seed germination. Since many of the published data of salt effects on seed germination use salinity of incubating solutions, salinity of the extract may have to be converted to that of the soil solution (Eq. [9]).

For many crops, stand problems begin after the seed has germinated. Hypocotyls emerging from the seed may have trouble passing through the soil layer above, which is often high in salts because of salt deposition occurring there during water evaporation. During this emergence process, hypocotyl mortality can occur, especially with crops sensitive to foliar salt damage. The levels of salinity that cause hypocotyl mortality vary widely. The levels are as low as 5 dS m^{-1} in EC_e of the top 5 mm of soil for guayule (*Parthenium argentatum* A. Gray), 10 dS m^{-1} for carrot (*Daucus carota* ssp. *sativus*) and more than 40 dS m^{-1} for tomato [*Lycopersicon lycopersicum* (L.)] (Miyamoto, 1986). One approach to handle this problem is to remove the surface crust of salts by mechanical means prior to seedling emergence (Miyamoto et al., 1986).

Emerged seedlings also undergo mortality when seedling roots are exposed to the highly saline zone typically present in the ridge region of furrow-irrigated beds or when substantial rain leaches the surface accumulated salts back into the seedling zone (Bernstein, 1974). Mortality of emerged seedlings also often occur when seedling leaves are exposed to saline splatters caused by light showers on salted soil surfaces (Miyamoto et al., 1986). However, rigid criteria to diagnose the extent of seedling mortality from those processes have not yet been fully developed.

Aside from the evaluation of salt damage to crops, salinity data obtained at different locations and depths in the field are useful for assessing irrigation efficiency and uniformity of water infiltration, and for estimating the leaching fraction (Rhoades, 1980).

B. Sodicity Hazard

The suitability of soils for cropping depends appreciably on their ability to conduct water and air (permeability) and on aggregate properties that control the friability of the seed bed (tilth). In contrast to saline soils, sodic soils have reduced permeabilities and poorer tilth. Sodidity adversely affects these physical properties of the soil and hence its suitability as a medium for crop growth. The direct effect of Na per se on crop growth is limited to a few crop species and is discussed later as a case of specific ion hazard (see section III.C).

The ESP has, in the past, been used to assess adverse Na effects. A classic criterion used for defining a sodic soil is an ESP value of ≥ 15 (U.S. Salinity Laboratory Staff, 1954). However, the presence of sufficient electrolyte can

counteract the adverse effects of Na. Thus, the problems traditionally associated with sodicity should be assessed only in conjunction with a consideration of the accompanying level of salinity.

A short-range adhesive force (commonly referred to as van der Waals force) is primarily responsible for the flocculation of clay particles. The adsorption of Na molecules on clay surfaces enlarges the thickness of the diffuse-double layer existing around clay particles, thus increasing the repulsive force between adjacent particles of like charge. A consequence is dispersion of clay particles and deterioration of soil structure. With increasing ESP (or SAR) beyond about 15, Na enters the interlayer positions between the parallel platelets of smectitic clay particles and brings about swelling (Shainberg & Letey, 1984). Increasing electrolyte concentration reduces the thickness of the diffuse layer inside the shear plane by forcing more ions into it by mass action and counteracts the dispersive and swelling effects of loosely absorbed Na ions.

These underlying mechanisms largely dictate the effects of sodicity and salinity on soil physical properties of practical importance. Hydraulic conductivity, for instance, generally decreases with increasing sodicity or decreasing salinity. When ESP is ≤ 15 , the slaking of aggregates and dispersion of clay particles and accompanying loss or continuity of water conducting pore space are the principal causes of reduced infiltration rate and hydraulic conductivity. As ESP exceeds 15, the swelling factor comes into greater play in soils, especially in those containing smectitic clays. The magnitude of reduction in hydraulic conductivity depends on soil properties. When the electrolyte concentration of percolating solution is 10 mmol_c/L, ESP that causes a 15 to 25% reduction in hydraulic conductivity ranges from 5 to 25 in soils of mixed mineralogy (McNeal & Coleman, 1966a, b; Quirk & Schofield, 1955; Frenkel et al., 1978). Hydraulic conductivity of soils often decreases even with ESPs of 5 when electrolyte concentration is lower than about 3 to 5 mmol_c/L (Shainberg, 1984). Under unsaturated flow conditions, sodicity causes lesser effects on hydraulic conductivity (e.g., Russo & Bresler, 1977). An approximate conversion between electrolyte concentration and EC was given earlier (see section I.C.4).

Water infiltration into soils is sensitive to ESP and electrolyte concentration as has been shown by the lysimeter data of Oster and Schroer (1979) and Miyamoto (1989). When water infiltrates into the soil surface, the soil solution of the topsoil is essentially that of the infiltrating water while the exchangeable Na percentage is essentially that pre-existent in the soil (since ESP is buffered against rapid change by the soil CEC). All water entering the soil must pass through the surface; hence, the stability of the topsoil aggregates influences the water entry rate of the soil. Representative threshold values of SAR (~ESP) and the electrical conductivity of infiltrating water for maintenance of soil permeability can be estimated from Fig. 12-12 (Rhoades, 1982b). Because significant differences exist in the Na-salinity response among soils, this relation should only be used as an approximate guideline. Reductions in water infiltration under rainfall or sprinkler and surface irrigation may be even more of a problem than is indicated in Fig. 12-12 because of enhanced particle dispersion and aggregate slaking caused

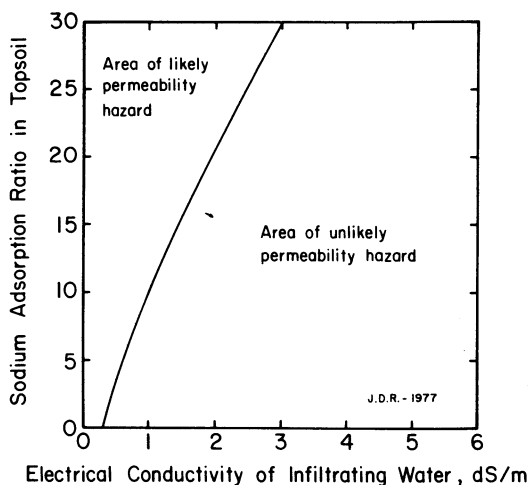


Fig. 12-12. Threshold value of sodium adsorption ratio (SAR) of topsoil and electrical conductivity of infiltrating water for maintenance of soil permeability.

by the energy of falling and flowing water (Oster & Schroer, 1979; Miyamoto, 1982; Shainberg, 1984). The dispersed particles form a “washed-in” layer of low permeability (Shainberg, 1984) and a crust through which seedlings have difficulty in penetrating during emergence.

Sodic soils can be improved with amendments such as gypsum, sulfuric acid, organic matter, and sulfur (Rhoades, 1982b; Stroehlein et al., 1978; Miyamoto et al., 1975; Stromberg & Tisdale, 1979). Generally, fast-acting amendments are expensive; slower ones are less so.

C. Specific Ion and Toxicity Effects

Certain salt constituents are specifically toxic to some crops. Boron is highly toxic to many crops when present in the soil solution at concentrations of only a few milligrams per liter (Maas, 1984; Keren et al., 1985; Bingham et al., 1985). In some woody crops, Na and chloride may accumulate in the tissue to toxic levels (Bernstein, 1974; Maas, 1984, 1985). These toxicity problems are not generally major ones. The effects of salinity and toxic solutes on the physiology and biochemistry of plants are discussed in more detail by Maas and Nieman (1978) and Maas (1984).

Sodic soil conditions may induce Ca and various micronutrient deficiencies by the associated high pH and bicarbonate conditions repressing their solubilities and thereby lowering their concentrations and, in the case of “heavy metals,” due to precipitation of hydrous oxides.

IV. SUMMARY

Soluble salts in soils can be determined or estimated from measurements made (i) on aqueous extracts of soil samples, (ii) on saturated soil pastes, and (iii) on the field soil. The latter measurements can be made using four-electrode probes, TDR probes or electromagnetic (EM) sensors. The appropriate method of measuring soil salinity should be selected for the specific condition and purpose. If only a measure of total soluble electrolyte level in the soil is needed, EM or four-probe devices are recommended. When determination of a particular solute is needed, then collection and extraction of soil samples is required. Soil sample extracts give relative comparisons only, because the soils are adjusted to unnaturally high water contents during extraction. A combination of the various methods minimizes the need for sample collection and chemical analysis, especially when monitoring salinity changes with time and characterizing large field or project situations. For this purpose, use of EM and four-probe field techniques are recommended with supplemental use of the other methods as needed. If soil samples are used in the field and only salinity is needed, the measurement of the saturated soil-paste is recommended.

The ESP of soils can be adequately estimated from the more rapid and simpler measurement of the SAR of the saturation extract. The sodicity hazard of a soil should be assessed from the combined values of estimated ESP, electrolyte concentration, and pH taking into consideration soil texture and clay mineralogy, along with the irrigation and tillage practices. The focus of attention should be the near-surface soil, in this regard.

While salinity and sodicity are the major factors limiting crop growth in most salt-affected soils, specific ion toxicities may be important in some cases. Special consideration should be given to Na and chloride, where woody, perennial crops are being grown and to B for susceptible crops.

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Chapter 13

Testing Artificial Growth Media and Interpreting the Results

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Testing containerized growth media provides many challenges and opportunities. Since the mid-1960s, growth media used for producing floral, vegetable, and ornamental plants in containers have changed from soil-based mixes to peat- and bark-based mixes. These changes in growth media composition have necessitated changes in testing procedures from those developed for soil to ones more suited for mixes of peat, bark, sand, or vermiculite. In the USA, a gradual change has occurred from the soil-oriented Spurway procedure to water-extraction methods. Use of the saturated media extract has increased among university and commercial testing laboratories. In the European countries, water extract methods have been in use for a longer period as have artificial growth media.

The many artificial growth media being used have been developed for improvement of drainage and aeration with nutrient-supplying abilities being considered second (Boodley & Sheldrake, 1972; Lucas & Rieke, 1968; Matkin et al., 1957; Whitcomb, 1984). Even though the peat, composted bark and vermiculite have nutrient-holding capabilities the nutrients are held less tightly than by mineral soils. Table 13-1 shows that a high percentage of N, P, and K added to two peat-based growth media remained recoverable by water extraction. The presence of expanded vermiculite in the medium did reduce the water-extractable K and NH_4 (Bunt, 1988). By being able to extract with 0.03 M acetic acid, 100% of the N, P, and K added to a sphagnum peat, Nowosielski and Beresniewicz (1957) demonstrated that the nutrients not recoverable by water extraction are not bond tightly by the substrates. All P and K added to a shredded pine bark was also 100% recoverable. Nitrogen recovery decreased to 30% after 12 wk of composting due to immobilization but increased to more than 100% after 6 mo of composting.

In soils, the capacity factor is extremely important for the continual supply of nutrients to plant roots. However, the importance of the intensity factor overshadows the capacity factor when plants are intensively grown in soilless media with frequent watering; periodically with a nutrient solution. As the content of soil in a growth media decreases, the importance of

Table 13-1. Percentage of added nutrients recovered in 1 L of leachate from peat-sand (75-25%) and peat-vermiculite (50-50%) composts. (Bunt, 1988).†

Element	Peat-sand	Peat-vermiculite
NH ₄ -N	81	33
NO ₃ -N	87	75
P	60	43
K	70	45

† Pot capacity was 1 L.

the capacity factor decreases while that of the intensity factor increases. The relative roles of the capacity and intensity factors are, therefore, an important consideration in developing an appropriate testing methodology for artificial growth media.

I. HANDLING AND PREPARING GROWTH MEDIA FOR TESTING

The prime objective in testing a growth medium, whether soil or soil-less, is to characterize the nutrient environment as closely as possible to the way the plant root system experiences it. Improper handling of a growth medium sample can greatly increase the difficulty of attaining this goal. Field soil samples are usually dried, ground, and sieved prior to testing, but it is recognized that drying, especially at temperatures $>38^{\circ}\text{C}$, may change extractable nutrient levels.

Grinding of samples usually helps facilitate a uniform sample for testing. However, some components of artificial media, such as expanded vermiculite, polystyrene beads, and calcined clay, do not grind well. The grinding and sieving process will give a uniform sample, but may also systematically alter both the chemical and physical properties of the original medium that could result in testing a material whose composition is different from the medium in which plants are grown. Grinding a medium that contains slow-release fertilizers generally increases the test levels. For these reasons, grinding of soilless growth media is not recommended. Sieving is also questionable as it may result in separation of constituent materials and the testing of a medium different from that used. Recognizing that artificial growth media are not homogenous, the best approach to collecting and testing a representative sample is to use as large a sample as practical.

Should the sample to be tested be measured by weight or by volume? Mehlich (1972, 1973) has presented a good discussion of this matter for field soils. Prime consideration must be given to the fact that plants grow in a volume of growth medium. The bulk density of growth media vary considerably, ranging from <0.2 to $>0.8 \text{ Mg m}^{-3}$. Cation-exchange capacity (CEC) values of low-density materials such as peat, composted barks, and vermiculite appear quite high when expressed on a weight basis. However, when expressed on a volume basis the CEC values are actually similar to or less than those of mineral soils (Brown & Pokorny, 1975; Bunt, 1988; Lucas, 1983; Whitcomb, 1984). For example, on a weight basis the CEC of

sphagnum peat, pine bark, and a loam soil are 1000, 440, and 120 mmol kg⁻¹, whereas on a volume basis the respective CEC values are 80, 110, and 150 mol m⁻³. Since many testing methods specify a given sample/solution ratio, measuring the sample by weight or volume will influence the test result and subsequent interpretation. Consider two growth media, A and B. Medium A has a density of 0.4 Mg m⁻³ and medium B has a density of 0.8 Mg m⁻³. Ten millimole of nitrate-N (NO₃-N) is mixed with 1 L of each medium. If each medium is extracted on a volume/volume (v/v) basis with a sample/solution ratio of 1:5, the extract from each will contain 2 mmol NO₃-N L⁻¹. However, when extracted on a volume/weight (v/w) basis at a ratio of 1:5, the extract of medium A will contain 5 mmol NO₃-N L⁻¹ whereas medium B will contain 2.5 mmol NO₃-N L⁻¹. Hence, samples measured on a weight basis will necessitate conversion of the results to a volume basis or require separate sets of interpretation guidelines based on medium density. In considering these factors, measuring and testing of growth media should be conducted on a volume basis.

Handling a container growth medium in a moist state provides the opportunity to test the medium in a condition similar to how it will be or was used. However, some changes may occur if the sample is maintained in the moist state for several days while being shipped to a lab for testing. Most concern is for N conversions that may occur, resulting in more or less available N. Furthermore, the distribution of NH₄ and NO₃ forms may change. The occurrence of more NO₃ would increase the soluble salt level by bringing more cations into solution. However, Markus and Steckel (1980) found the NO₃ and NH₄ content did not change in moist media held in airtight containers at 7 or 22 °C for 3 and 6 d. Hence, the concern for N conversions may not be as serious as commonly thought. If a growth medium contains slow-release fertilizer, maintaining it in a moist state for several days may result in some inflation of the test results due to continued nutrient release. But drying and rewetting these media may actually result in greater nutrient release from the slow-release fertilizers. And complete drying of growth media may alter the ionic equilibrium (Jackson, 1958). Some soluble nutrients may precipitate in forms not readily solubilized when rewetted during extraction. Peat-based media rewet slowly after being dried and some researchers have found use of a surfactant helpful in rewetting them (White et al., 1975). Even then complete wetting may not occur during the extraction times used in many testing labs. Markus (1986) extracted higher amounts of P, K, Ca, and Mg from moist samples compared with samples that were air dried. Hence, maintaining media samples moist prior to testing appears to be best.

II. ANALYTICAL APPROACHES

With frequent watering and fertilization of container-grown plants, the importance of exchangeable cations and immobilized nutrients in the growth media is diminished. Analytical procedures must reflect the nutrient environ-

ment of the root system. The concentration (intensity) and balance of the nutrients in the solution phase is important in these weakly buffered systems. While an analytical method must provide accuracy and reproducibility, Bunt (1986) has pointed out that for use in a service lab a method should also: (i) allow for handling several samples per day; (ii) incorporate simplicity to be independent of individual operator skill; and (iii) be suitable for analyzing a diverse range of materials. Furthermore, for extension purposes the analytical procedure must provide results related to plant growth responses and be backed up with interpretation and recommendation guidelines.

Slow-release fertilizers are frequently used to help maintain adequate nutrient concentrations in artificial growth media and this provides an additional challenge for analysis. Ideally, the procedure will be able to determine the nutrient status of a medium containing slow-release fertilizer without stimulating additional nutrient release.

Several different analytical methods are being used for analysis of artificial growth media used for container-grown plants. Bunt (1986) classified these into three categories: (i) suspensions extracted with water, acids, or salts; (ii) saturated media extracts; and (iii) displaced soil (media) solutions.

A. Acid Extracts

1. Suspensions

Since 1940, perhaps the most popular system for analyzing greenhouse soils and soil mixes in the USA has been the method developed by C.H. Spurway during the late 1930s and early 1940s (Spurway, 1943; Spurway & Lawton, 1949). The Spurway method originally used 13 mL of 0.018 *M* acetic acid to extract plant-available nutrients from 4 cm³ of mineral soil. Later, some labs modified the method by: (i) using a different medium/solution ratio; (ii) weighing out the sample; and (iii) using other extractants for N and the cations. Surveys of soil testing labs in the mid-1970s indicated the modified Spurway system was being used widely for analysis of both soil-based and soilless growth media. The Spurway system has the advantage of considerable background calibration data and interpretation guidelines for a wide spectrum of plant species. Hence, extension horticulturists have felt comfortable with data generated via this methodology. Several samples can be handled quickly, but, on the other hand, the medium is dried prior to being analyzed and, in some labs, several extractions are used for a complete analysis. The small sample size makes representative sampling of heterogeneous growth media difficult. When the Spurway method is used to extract media containing slow-release fertilizer, the test values are inflated rather than reflecting the current available nutrient status. Several other acid and salt extractions have been evaluated by Markus and Steckel (1980). The Mehlich I (double acid) extracted the largest quantity of nutrients, but no one extractant was superior to the others as a diagnostic tool. Several of the extractants correlated well with each other in the extraction of various

nutrients, but correlation with nutrient uptake by plants was not good for any of the extractants studied. Sartain (1983) found that Mehlich I analyses were less variable than other methods, but again nutrient uptake by tomato (*Lycopersicon esculentum* Mill.) did not correlate with nutrient levels extracted by Mehlich I.

B. Water Extracts

1. Suspensions

Water extraction is used in western Europe where soilless potting media are used predominantly (Bunt, 1986). Saturated media extracts and displaced solutions are used in research, but water suspension extracts are used by service laboratories. Johnson (1980) found water extracts at various medium/solution ratios, ranging from 1:1.5 to 1:6, gave more consistent results than did chemical extractants. Based on Johnson's studies, the Agricultural Development and Advisory Service (ADAS) of the United Kingdom routinely analyzes all potting media using a 1:6 (v/v) medium to pure water ratio.

The development of water extract procedures has faced two main concerns: (i) whether to use moist or dry samples, and (ii) whether to prepare extracts on a weight (w/v) or volume (v/v) basis. Some concerns regarding air-drying samples prior to extraction are presented in section I. Extraction of moist samples presents the problem of variation in the initial moisture content. Sonneveld and van den Ende (1971) adjusted all mineral soil samples to field capacity before making a one part soil to two parts water (v/v) extract. Conductivity and soluble nutrient levels obtained with this approach agreed much better with saturation extract data than data obtained with 1 part soil to 25 parts water (w/v). The variability in moisture-holding capacity is greater among artificial growth media than among mineral soils. Hence, making suspension extracts without regard for the initial moisture content would give variable results. Johnson (1980) found that by using a wide medium to water ratio, i.e., 1:6, this problem could be overcome. However, as the extraction ratio increases the resulting conductivity values and nutrient levels become less agreeable with saturation extracts (Sonneveld et al., 1974). Dutch researchers have shown variability in the moisture content of growth media is minimized by adjusting the moisture tension to pF 1.5 (about 32 cm of water). They reported this adjustment can be made visually with experience, but periodic checks on a sand box are desirable. Another source of variability with volume extracts is the quantity packed into a unit volume. In preparation for their 1:1.5 (v/v) extracts, Sonneveld et al. (1974) and Johnson (1980) used a constant pressure of 0.1 kg cm^{-2} . Thus, by standardizing the moisture tension and the pressure used in measuring a specified volume, their analytical results correlated very well with those in the medium solution extracted with a hydraulic press; $r^2 = 0.96$ or better (Table 13-2). Nutrient concentrations in the 1:1.5 extract were 20 to 33% the concentration in the press extract.

Table 13-2. Regression equations for relationships between analytical data of press extract (x) and 1:1.5 volume extract (y) Sonneveld et al. (1974).

Determination	Regression equation	r
Conductivity	$y = 0.311 x - 0.05$	0.969
Cl	$y = 0.218 x + 0.17$	0.975
N	$y = 0.256 x + 0.02$	0.967
NO ₃	$y = 0.239 x + 0.18$	0.961
NH ₄	$y = 0.280 x + 0.17$	0.986
PO ₄	$y = 0.270 x + 4.04$	0.972
K	$y = 0.302 x + 0.17$	0.982
Mg	$y = 0.298 x - 0.75$	0.957

2. Saturated Media Extract

Under conditions of equilibrium, the composition of the solution phase of the growth medium fully characterizes the root environment. Lagerwerff (1958) documented this statement by demonstrating that nutrient uptake was similar from the solution and adsorbed phases. In weakly buffered growth media, the concentration of nutrients in solution will be of greater importance than in well-buffered mineral soils. The saturation extract method was first developed for determining total soluble salt levels in soils (Richards, 1954), but is useful in determining specific soluble nutrient concentrations in weakly buffered artificial growth media. Geraldson (1957, 1967) found that saturation extracts reflected well the available nutrient status of very weakly buffered coarse sands in Florida. Following Geraldson's lead, Lucas et al. (1972) studied the feasibility of using a saturated medium extract (SME) procedure for routine analysis of potting media. Results obtained with the SME method agreed well with those obtained with the modified Spurway system (Table 13-3).

The SME method used by the Michigan State University Soil Testing Laboratory is described in North Central Regional Bull. 221 (Warncke, 1988). Basically, 400 cm³ of growth medium (just as it comes to the lab) is mixed with additions of pure water until it is just saturated. After equilibrating for 1.5 h, pH is determined in the saturated medium and the solution is extract-

Table 13-3. Correlation of test variables determined by the SME method and modified Spurway extraction procedure.†

Test	r Value	Extractant
Soluble salts	0.99	0.018 M HOAc
NO ₃ -N	0.97	0.018 M HOAc
P	0.90	1.0 M NH ₄ OAc
K	0.90	1.0 M NH ₄ OAc
Ca	0.57	1.0 M NH ₄ OAc
Mg	0.59	1.0 M NH ₄ OAc
Na	0.35	1.0 M NH ₄ OAc
Zn	0.94	0.1 M HCl
Mn	0.98	0.1 M HCl
Cu	0.70	1.0 M HCl

† Samples of growth media were collected from several greenhouses in Michigan. Original paper by Lucas et al. (1972) does not indicate sample numbers or replications.

Table 13-4. Influence of increasing water volume on the soluble salt and nutrient levels in the saturation extract.

Water volume†	Soluble salts	NH ₄ -N	P	K	Ca	Mg
L	relative value‡					
0.175	1.18	1.29	1.13	1.14	1.34	1.18
0.200	1.15	1.22	1.04	1.07	1.25	1.16
0.225	1.00	1.00	1.00	1.00	1.00	1.00
0.250	0.97	0.87	0.87	0.93	0.94	0.93
0.300	0.79	0.71	0.65	0.79	0.81	0.80

† Volume of water mixed with 0.40 L of Redi-earth. Saturation was attained near 0.225 L of water.

‡ Actual test values equal to 1.00 were: 1.70 dS m⁻¹; 7 mmol NO₃-N L⁻¹ 0.23 mmol P L⁻¹; 0.36 mmol K L⁻¹; 1.7 mmol Ca L⁻¹; and 4.87 mmol Mg L⁻¹.

ed with a vacuum filter, and all subsequent analyses are conducted on the filtrate. This approach overcomes several problems associated with analyzing artificial growth media: (i) large samples can be analyzed without preparatory drying and handling which minimizes the concern for segregation or heterogeneity of components; (ii) since only gentle mixing is involved, medium containing slow-release fertilizer can be analyzed with only minimal and insignificant effects on test values (Warncke, 1986); (iii) only one set of interpretation guidelines is needed; and (iv) calculation of nutrient balance is possible.

Results obtained by the SME method have been more variable than with other methods (Holcomb & White, 1979, Sartain, 1983; Warncke, 1983). Much of the variability is associated with the difficulty of accurately mixing the medium to the point of saturation. With field soil, the criteria for determining the endpoint are relatively clear: (i) the soil just begins to flow; (ii) the soil surface glistens; and (iii) the soil slides cleanly off a spatula. Many potting media will also mix easily and flow slightly at the saturation endpoint. As the content of fibrous peat, coarse bark, polystyrene beads, and similar materials increases, however, the difficulty of accurately determining the endpoint increases. Table 13-4 illustrates how missing the saturation endpoint affects the relative nutrient concentrations in the extract. Deviation of the relative nutrient values from those obtained at saturation was less by adding excess water than by undersaturating the medium, except for P. When expressed as a percentage of the total soluble salts, Warncke (1986) has shown variability of test results is much less than when absolute nutrient concentrations are considered.

Michigan State University started using the SME method for routine analysis of artificial growth media in 1974. Since then, many service laboratories across the USA and Canada have adopted the method. Admittedly, the SME method is time consuming and does not lend itself to doing 40 000 samples per year, as is done by some advisory centers in western Europe. However, some labs in the USA are using the SME method and handling 3000 to 4000 samples per year.

Table 13-5. Summary of nutrient levels in saturation extracts with various extractants.†

Nutrient	Extractant				
	Water	1M NH ₄ OAc	Bray 1	0.02 M HOAc	0.1 M HOAc
	mmol L ⁻¹				
P	0.74	0.64	1.61	0.84	1.13
K	2.63	4.40	--	2.61	2.86
Ca	5.55	20.27	--	8.10	13.12
Mg	4.08	14.29	--	5.91	8.67
Zn	0.007	0.011	0.006	0.012	
Mn	0.014	0.052	0.033	0.021	0.038

† Average values for nine growth media.

There is some concern as to how well nutrient concentrations in water extracts relate to overall nutrient availability in growth media. Warncke (1986) compared SME with other common extractants on nine commercial growth media. Results in Table 13-5 show water-extractable P and K levels compared closely with the active Spurway extractant (0.018 M acetic acid). Some additional P and K was extracted with the Bray and Kurtz P₁ and ammonium acetate extractants. The water-extractable cation levels being proportionate to NH₄ acetate extractable levels indicates the SME water-soluble nutrient concentrations reliably reflect the plant-available nutrient status of growth media.

3. Displaced Solution

Parker (1921) demonstrated that the equilibrium soil solution could be accurately displaced by adding water or another liquid to a soil column. The water added to the top of the column acts as a plunger to force the soil solution out the bottom. The nutrient concentration in the displaced solution was found to be inversely proportional to the moisture content of the soil. As Nelson and Faber (1986) increased the medium moisture tension from 0 to 15 kPa, the NO₃-N concentration in the displaced solution increased from 38 to 148 mmol L⁻¹. Burd and Martin (1923) demonstrated that an accurately displaced solution is truly representative of the soil solution. Uniform packing of columns is key to obtaining a true displaced solution. Growth media composed of several components are more difficult to pack to prevent channeling than soil. To deal with this potential problem, Faber and Nelson (1984) packed 1000 cm³ of medium, 100 cm³ at a time, into a 5-cm diam. and 60-cm tall column, and then displaced the medium solution using an aqueous solution of 5% potassium thiocyanate in 50% ethanol. Any intermixing of the displacing solution with the medium solution was detected by testing the displaced solution with 0.5% ferric chloride. Formation of the bright-red ferric thiocyanate indicated intermixing had occurred. The column displacement methodology has proven to be useful in research; however, the detail of the procedure precludes its use for routine diagnostic analyses.

4. Pour-Through

A variation of the displaced extract and saturated media extract is the Pour-Through (PT) method (Wright, 1986). The objective of the PT method is to displace the medium solution, which is in equilibrium, by adding water to the container. The growing plant is not disturbed with this approach. Water must be added to the center of the container to avoid channeling down along the sides. Adding excess water can cause dilution and misleading results. Yeager et al. (1983) determined that 40 to 100 mL of water can be added to a 1-gal container without affecting the nutrient concentration in the extract. As with true displaced extracts, the moisture content of the medium at the time of extraction influences the final nutrient concentrations. A standard initial moisture content is essential for development of interpretation guidelines. Wright (1986) suggests the medium moisture content be near container capacity, however, this may be too saturated. Extracting a set time after watering is desirable to allow for equilibration of the water with the medium. The PT method lends itself nicely to monitoring pH and nutrient levels of media in large (1 gal size or larger) containers such as those used for nursery stock. For pot and bedding plants grown in smaller containers or cell-paks accurately obtaining an adequate volume of extract without dilution is difficult.

Holcomb et al. (1982) have demonstrated that medium solution can be extracted from smaller intact pots or containers by directly subjecting them to a 0.103 MPa (15 psi) vacuum. Nutrient concentrations in these extracts correlate well with those obtained with the SME method. The relationships for conductivity values (dS m^{-1}) and extractable K (mmol of K L^{-1}) were: $C_{se} = 1.55 C_{ve} + 0.61$ and $K_{se} = 1.60 K_{ve} + 0.002$ where se = saturation extract and ve = vacuum extract. Extracting small containers of media by the PT or vacuum approach at a specific length of time (12–24 h) after watering improves the consistency of results.

III. TESTING CONSIDERATIONS

Producing plants in containers requires intensive management and monitoring of the growth medium pH, soluble salts content, and essential nutrient concentrations. The appropriate levels of each is influenced by kind of growth medium, plant species being grown, and growth stage.

A. Growth Medium pH

Changes in the availability of essential plant nutrients in growth media with changes in pH are well documented in the literature. In moderately weathered mineral soils, the optimum pH range for overall nutrient availability is 6.5 to 6.8 (Truog, 1948). However, in highly weathered and leached mineral soil, the most suitable pH may be lower. In organic (peat) soils, Lucas and Davis (1961) found the best pH range for overall nutrient availability

Table 13-6. Effect of mineral soil content on interpretation of growth media pH. Adapted from Peterson (1984).

Interpretation	Soil mix (>20% mineral soil)	Soiless mix (<20% mineral soil)
	pH	
Very low	5.0-5.4	4.4-4.7
Low	5.5-5.9	4.8-5.1
Slightly low	6.0-6.4	5.2-5.4
Optimum	6.5-6.8	5.5-6.0
Slightly high	6.9-7.2	6.1-6.5
High	7.3-7.4	6.6-6.9
Very high	7.5-7.6	7.0-7.3
Extremely high	7.7-8.4	7.4-7.8

to be 5.5 to 5.8. Since many artificial media are peat-based, the most suitable pH should be closer to 5.5 than to 6.5. Working with one such peat-based growth medium, Peterson (1981) demonstrated that overall nutrient availability was maximal between pH 5.3 and 5.5. Markus (1986) found extractable Cu and Mn were maximal between pH 5.5 and 6.0. As growers have switched from soil to peat-based media, problems have surfaced because they have not recognized that the optimum pH may also have changed. Table 13-6 provides an interpretation guide of pH for growth media with high and low mineral soil content. Optimal pH values for growth media containing composted barks vary with the bark source, softwood or hardwood (Nelson, 1987; Whitcomb, 1984).

The pH of a saturated growth medium reflects closely the pH within the root zone. pH values determined using one part medium to two parts pure water may be 0.5 or more pH units higher than that determined in the saturated medium. Since much of this difference may be due to salt effect, pH values using 0.01 *M* calcium chloride relate more closely to pH's determined by placing the pH electrodes in the saturated medium. Hipp et al. (1979) found pH values of solutions obtained by placing porous ceramic cups into pots of medium agreed quite well with those in saturated medium and could be expressed by $Y = 0.99 X + 0.20$ ($r = 0.96$) where *Y* is the solution pH and *X* is the saturated medium pH. Further study revealed that pH values obtained by placing pH electrodes in direct contact with the medium surface in a container, with plants growing, gave results that were less acceptable than those obtained with the ceramic cups. Measuring the pH in solution extracts must be done carefully because the solution extract from most container growth media is weakly buffered, and pH values may be easily altered by contamination.

B. Conductivity (Soluble Salts)

The value of conductivity (soluble salts) measurements as a diagnostic aid in obtaining good plant growth has been demonstrated over the years by several researchers (Merkle & Dankle, 1944; McCall et al., 1961; Mascianica, 1983). Soluble salts are determined by a measure of electrical con-

ductance of a solution and is a summation of contributions from all the ions present, both cations and anions. The degree of conductance is influenced by the number of ions per unit volume of the solution and the velocities at which these ions move under the influence of applied electromotive force. The total soluble salt content of an extract solution is measured with a conductivity meter or solu-bridge. At 25 °C, a 0.010 *M* potassium chloride solution gives a conductivity reading of 1.41 dS m⁻¹. Soluble salts increase the osmotic potential of the medium solution, thereby affecting water and nutrient uptake by plant roots. Higher soluble salt levels are permissible in peat-containing media because they hold more water per unit volume than mineral soils (Fig. 13-1).

The soluble salt content of a growth medium is affected by the amount of ionized salts it contains. Fertilizers differ in their “salt index” depending on the degree of dissociation and subsequent effect on the osmotic pressure of a solution. Table 13-7 lists the salt indice and relative salinity of commonly used fertilizer materials.

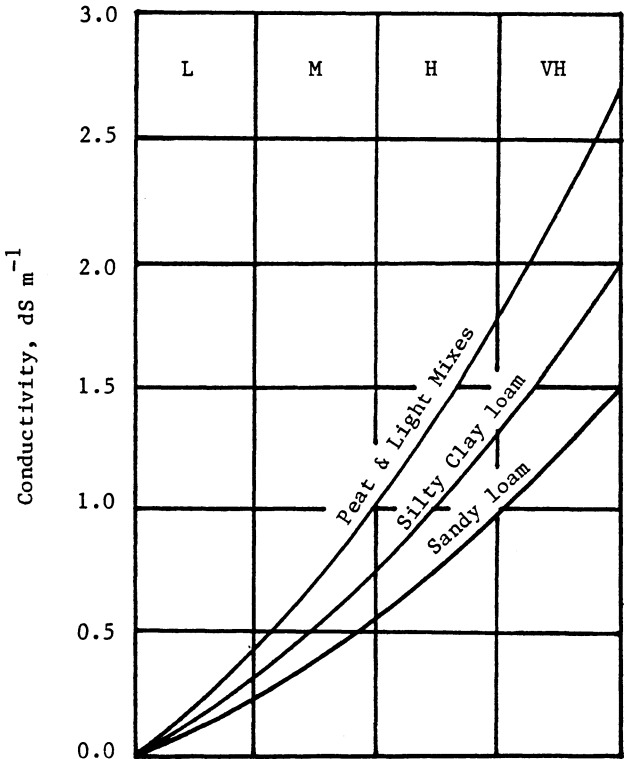


Fig. 13-1. Conductivity (soluble salt) ratings by the 1:2 (v/v) method for three growth media. Low (L): Needs additional fertilizer. Salt effect on plant is negligible. Medium (M): Can be fertilized lightly if in the lower end of the range, but is satisfactory near the top. High (H): Satisfactory in the lower end of the range, but germination and seedling injury may occur at the top. Very High (VH): Do not allow media to become dry or add fertilizer. Water enough to cause some leaching if near the top of the range. Leach extensively if over this range. (Modified from “Crop fertilization based on North Carolina soil tests.” Agronomic Div., North Carolina Dep. of Agric., Raleigh.

Table 13-7. Effect of fertilizers on the salinity of growth media. Adapted from Bunt (1988).

Fertilizer	Elemental content	Salt index†	Total nutrients‡	Relative salinity§
	%		%	
Sodium nitrate, NaNO ₃	16.5 N	100.0	16.5	100.0
Ammonium nitrate, NH ₄ NO ₃	35 N	104.7	35.0	49.4
Ammonium sulphate, (NH ₄)SO ₄	21 N	69.0	21.0	53.7
Ammonia solution, NH ₃	82 N	47.1	82.0	9.4
Calcium nitrate, Ca(NO ₃) ₂	11.9 N	52.5	28.8	30.1
Urea, CO(NH ₂) ₂	46 N	75.4	46	26.7
Diammonium phosphate, (NH ₄)HPO ₄	21 N, 23 P	34.2	44	12.7
Monoammonium phosphate, NH ₄ H ₂ PO ₄	12 N, 27 P	29.9	39	12.7
Superphosphate (triple), Ca(H ₂ PO ₄)·H ₂ O	19.6 P	10.1	19.6	8.5
Potassium chloride, KCl	49.8 K	116.3	49.8	38.5
Potassium nitrate, KNO ₃	13 N, 38 K	73.6	51	23.6
Potassium sulphate, K ₂ SO ₄	45 K	46.1	45	17.0
Calcium carbonate, CaCO ₃	40 Ca	4.7	40	1.9
Calcium sulphate, CaSO ₄	23 Ca	8.1	23	5.8
Magnesium oxide, MgO	60 Mg	1.7	60	0.5
Magnesium sulphate, MgSO ₄	16 Mg	44.0	16	44.5
Dolomite, CaCO ₃ + MgCO ₃	24 Ca, 12 Mg	0.8	36	0.4

† The "salt index" was calculated from the increase in osmotic pressure by equal weights of fertilizers relative to sodium nitrate.

‡ Total nutrients have been recalculated from the sum of the N, P, K, Ca, and Mg as usually stated in the fertilizer analysis, e.g., monoammonium phosphate = 12 N + 27 P = 39.

§ Relative salinity has been calculated from the increase in osmotic pressure per unit of plant nutrient relative to sodium nitrate.

The most common methods for measuring soluble salt content of growth media is to mix one part of media with two or five parts pure water. The 1:2 ratio is preferred, but 1:5 is necessary when the medium holds large amounts of water. These ratios have been used on a v/v and w/v basis. Unless the sample is completely air dried, the resulting soluble salt value will be influenced by the moisture content of the medium on either basis. A lack of standardization has, at time, led to some confusion (Kirven, 1986). Waters et al. (1970) found the 1:2 v/v method gave values that related better to plant growth than did the 1:2 w/v method. This is reasonable because plants grow in a volume of medium. With the density of growth medium varying considerably, a given weight of a heavy medium will give a much smaller volume than will a light-weight medium. In an analysis of 27 growth media, Waters et al. (1970) showed that soluble salt levels determined by saturation extraction (SME method) were superior in relating to plant growth to those obtained by the 1:2 v/v method. Table 13-8 shows guidelines for soluble salt levels obtained by the three methods used most frequently.

A concern with the 1:2 and 1:5 ratios is the solubilization of slowly soluble compounds, e.g., calcium sulfate or slow release fertilizers. Solubiliza-

Table 13-8. Soluble salt guidelines for growth media by three test methods. (Warncke & Krauskopf, 1983).

Saturated media extract	One part growth media to:†		Interpretation
	Two parts water	Five parts water	
	dS m ⁻¹		
0.0-0.74	0.0-0.24	0.0-0.12	Very low salt levels. Indicates very low nutrient status.
0.75-1.99	0.25-0.49	0.13-0.34	Suitable range for seedlings and sensitive plants.
2.00-3.49	0.50-0.99	0.35-0.64	Desirable range for most established plants. Upper range may reduce growth of some salt-sensitive plants and seedlings.
3.50-5.00	1.00-1.49	0.65-0.89	Slightly higher than desirable. Loss of vigor in upper range. Okay for high nutrient-requiring plants.
5.00-6.00	1.50-1.99	0.90-1.10	Reduced growth and vigor. Wilting and marginal leaf burn.
6.00+	2.00+	1.10+	Severe salt symptoms—wilting. Crop failure.

† Measured out on a v/v basis.

tion of these materials will give an inflated test value for soluble salts. Hence, use of the saturation extract approach is encouraged whenever possible.

C. Elemental Variables

1. Nitrogen, Ammonium, and Nitrate

The quantity and form of N present in growth media may significantly affect the quality and rate of plant growth. Excess N will produce rapid soft growth that results in poor quality. Most containerized plants grow best with most of the N in the NO₃ form, and excess NH₄ tends to depress the uptake of other cations, especially Ca. Ammonium toxicity may become apparent in some plants when NH₄ composes more than 30% of the soluble N fraction or makes up more than 3% of the total soluble salts (Bunt, 1988).

Solution NO₃-N content correlates well with leaf N content and plant growth (Gilliam & Wright, 1977). However, the most suitable concentration of NO₃-N in solution varies with composition of the medium. Prasad (1980) found that media containing barks and wood shavings tend to retain N, but peat-based media do not. Hence, soluble NO₃-N levels need to be higher in bark-based media to produce equal growth to peat-based media (Prasad et al., 1981a, 1983).

Generally, it is suggested that samples of moist growth media be extracted immediately or be refrigerated to prevent changes in the N status. However, as pointed out in section I, in working with peat-vermiculite mixes Markus and Steckel (1980) found no change in the NO₃ and NH₄ status when the media was held in air-tight containers for 3 and 6 d at both 7 and 23 °C.

Table 13-9. Correlation coefficients between extractable P by three methods and P uptake by cyclamen grown in three media. Adapted from Prasad et al. (1983).

Method	Medium					
	Bark		Peat		Peat + soil	
	T max†	R ² ‡	T max	R ²	T max	R ²
SME	0.52 (16)	0.949	1.10 (34)	0.872	0.19 (6)	0.880
1:1.5	0.13 (4)	0.929	0.39 (12)	0.864	0.10 (3)	0.987
Spurway	2	0.948	4	0.863	2	0.910

† T max = Test value at which maximum P uptake occurred. For SME and 1:1.5 T max is in mmol L⁻¹ (mg P L⁻¹). For Spurway T max is in mg kg⁻¹.

‡ R² = correlation coefficient between medium test values and P uptake.

2. Phosphorus

Extractable P varies with the composition of the growth media. Fibrous peats retain little P initially, but P retention increases as the peat decomposes (Lucas, 1983). Mineral soils, composted barks and wood shavings retain P quite well. When equal amounts of P are equilibrated with mixes containing the various components extractable P is highest in peat-based media; but all of them supply enough P for optimum plant growth (Prasad et al., 1983; Warncke, 1976).

Prasad et al. (1983) found that P uptake by cyclamen (*Cyclamen persicum* Mill.) and poinsettia (*Euphorbia pulcherrima* Willd.) grown in peat, bark, or peat + soil medium correlated well with P extracted by the SME, 1:1.5, and Spurway methods. However, the level of extractable P at maximum P uptake varied with the extraction method (Table 13-9). Some of the differences are accounted for by the Spurway values being reported as mg of P/kg of medium, whereas the SME and 1:1.5 values are mmol of P L⁻¹ (mg of P L⁻¹) extract. The test value required for maximum P uptake was higher for peat than for bark or peat + soil. Hence, the optimum P test value varies with the extraction method and composition of the growth medium.

3. Potassium

In many potting media being used today, K, being held rather loosely on the limited exchange sites, is easily displaced by the divalent cations, Ca and Mg. Prasad et al. (1981e) found water and ammonium acetate extractable K to be linearly related for several growth media of varying composition. Even though ammonium acetate extracted more K, the correlation between extractable K and plant uptake was similar for both extractants. Hence, the K content of the solution phase characterizes the K environment of the root quite well.

Retention of K among the various growth media components is less variable than P retention. Peats and expanded vermiculite retain K slightly better than wood wastes (Prasad, 1980). Both vermiculite and wood materials supply significant amounts of K for plant growth (Markus & Flannery, 1983; Prasad et al., 1981e).

4. Calcium and Magnesium

Plant availability of Ca and Mg in artificial growth media has received little study. Since divalent cations are bound more tightly within growth media than monovalent ions, water extracts do not reflect the available status of Ca and Mg as well as for K. Exchangeable Ca and Mg would be more reflective of the availability within the root environment. Verloo (1980) found that adequate Ca helped keep humic complexes flocculated and thereby maintained good physical condition of organic materials.

5. Sodium and Chloride

Determination of the Na and Cl content of containerized growth media is important because of their potential adverse effects on plant growth both directly and indirectly. Both contribute to the total soluble salt content of the medium solution. Sodium held on the exchange sites presents less potential consequence, although it may displace other essential cations and also compete for uptake sites on plant roots. Individually, Cl is of more concern because of its toxic effects at high concentrations. In solution culture, Geraldson (1970) found that vegetable plant growth was not adversely affected as long as the Na or Cl each accounted for < 10% of the total soluble salts in solution.

6. Micronutrients

Commercially prepared peat-based growth media are quite low in available micronutrients unless they have been added to the media. A summary of saturation extracts of peat-based media by the Michigan State University Soil Test Laboratory revealed that Zn and Mn concentrations in saturation extracts were below $0.004 \text{ mmol L}^{-1}$ (0.25 mg L^{-1}) and $0.006 \text{ mmol L}^{-1}$ (0.35 mg L^{-1}) in 74 and 82% of the samples, respectively. Composted barks are reported to contain adequate Zn and Mn, but are low in Cu. With micronutrient concentrations in saturation extracts being quite low and the range being narrow, development of interpretation guidelines has been difficult. When Berghage et al. (1987) substituted various acids, salts, or chelates for water in the SME method, they were able to significantly increase the levels of Zn, Mn, and Fe in the extract. 0.005 M of diethylenetriaminepentaacetic acid (DTPA) was selected for modification of the SME method because it had minimal effects on the other variables and uptake of Zn, Mn, Fe, and Cu related well to extracted levels (Berghage, 1986). The DTPA improved the extraction of the cationic micronutrients in peat, peat/pine bark, and soil-based media. DTPA used as an extractant of micronutrients seems reasonable since Verloo (1980) has shown peat and peat decomposition products complex micronutrients. Using Mehlich I and DTPA extractants at medium to extractant ratios of 1:5 and 1:4 (v/v), Markus et al. (1981) increased the amount of Zn, Mn, Fe, and Cu extracted from peat-vermiculite media. Extracted Zn and Mn levels correlated well with concentrations in tomato leaf tissue.

Table 13-10. Estimated optimum P values based on maximum plant dry weight of cyclamen for three methods of extracting P from peat, bark, and peat + soil (Prasad et al., 1983).

Test method	Substrate	R^2 †	Optimum level‡
1:1.5	Peat	0.422	0.26-0.28 (8.1-8.8)
SME	Peat	0.504	0.79-0.86 (24.5-26.7)
Spurway	Peat	0.559	3.2-3.5
1:1.5	Bark	0.432	0.12-0.13 (3.7-4.0)
SME	Bark	0.546	0.45-0.48 (13.9-15.0)
Spurway	Bark	0.525	1.4-1.6
1:1.5	Peat + soil	0.420	0.045-0.061 (1.4-1.9)
SME	Peat + soil	0.464	0.074-0.119 (2.3-3.7)
Spurway	Peat + soil	0.438	0.9-1.2

† Correlation coefficient between plant dry weight and extractable P.

‡ SME and 1:1.5 values are mmol L⁻¹ (mg L⁻¹). Spurway values are mg kg⁻¹.

IV. INTERPRETATION OF TEST RESULTS

Methods for extraction of nutrients are easily developed. However, the success of an extractant for nutrient evaluation depends on a direct and predictable correlation with plant uptake, growth, or quality. This relationship can then be used in the development of good interpretation guidelines that are essential for an extraction method to be used as a useful diagnostic tool.

Prasad et al. (1983), studying the effects of nutrient levels on growth of cyclamen and poinsettia, found that test values from three separate methods correlated equally well with nutrient uptake. Regression equations for each of the three extracting methods (1:1.5; SME; and Spurway) were quadratic for N, P, and K. Plants grown in bark and similar mixes that retain N take up less N than plants grown in peat (Prasad et al., 1981b, 1983). Although there were differences in N uptake, the desirable N levels in the peat and bark media were similar, with the bark values being slightly higher. Nitrogen levels that produce the best growth and quality may vary greatly with plant species. The optimum N concentrations in the extract by the 1:1.5 method were found to be near 11.7, 4.4, and 17.2 mmol L⁻¹ for mums, (*Chrysanthemum morifolium* Ramat.), verbena [*Aloysia triphylla* (L'Hér.)] and tomato, respectively.

As illustrated in Table 13-10, P levels desirable for optimum plant growth vary considerably with the composition of the growth media (Prasad et al., 1981c, d, 1983). Across all three test methods compared, maximum P uptake occurred with quite low P concentrations in the extract when mineral soil was included in the growth media. Similarly, maximum P uptake was achieved from bark-based media at much lower test values than from peat-based media. Apparently, some of the plant-available P is held by soil and bark in forms not readily extracted with water or weak acetic acid (Spurway extractant). However, these forms are in direct equilibrium with the water-soluble P. In these studies, the R^2 values were lower when based on plant dry weight than on P uptake.

Table 13-11. Standard values for total soluble salts content and nutrient levels in extracts of growth media obtained by the 1:1.5 and SME methods.†

Analytical value	Unit	Optimum		Very high	
		1:1.5	SME	1:1.5	SME
Conductivity‡	dS m ⁻¹	1.3-1.8	2.0-3.5	3.6+	5.0+
NO ₃ -N	mmol L ⁻¹	3.7-5.4	7.1-13.2	9.0+	21.4+
P	mmol L ⁻¹	0.48-0.68	0.23-0.42	1.13+	0.61+
K	mmol L ⁻¹	1.5-2.1	4.0-6.0	3.5+	9.0+
Ca	mmol L ⁻¹	--	2.5-5.0	--	12.5+
Mg	mmol L ⁻¹	0.65-0.90	1.5-3.0	1.5+	7.25+
Na	mmol L ⁻¹	--	<3.0	--	13.6+
Cl	mmol L ⁻¹	<3.3	<2.5	6.7+	5.7+

† Data compiled from Bik and Boertje (1975), Peterson (1984), Sonneveld et al., (1974), and Warncke and Krauskopf (1983).

‡ Specific conductivity of the extract at 25°C.

In contrast to N and P, the relationship between K uptake and test values are similar for peat- and bark-based growth media. Several test methods predict K uptake equally well (Prasad et al., 1981e, 1983). Potassium test values for optimum uptake and plant growth were near 3.0 and 4.1 mmol L⁻¹, and 1.0 mg kg⁻¹, respectively, for the 1:1.5, SME, and Spurway methods.

Limited studies at the Horticulture Research Center in Levin, New Zealand indicate that a factor of 2.5 to 3.0 can be used to convert Spurway test values to 1:1.5 (Dutch Method) test values (Prasad et al., 1983) on peat and bark media. Studies by Bik and Boertje (1975) indicate that the relationship between conductivity values (dS m⁻¹) determined by the 1:1.5 and SME methods can be expressed as $EC_{(1:1.5)} = 0.384 EC_{(SME)} + 0.012$. They also found that the relationship between NO₃-N test values (mmol L⁻¹) by the two methods was represented by $N_{(1:1.5)} = 0.38 N_{(SME)} + 1.14$. These equations illustrate that nutrients are more concentrated in saturation extracts due to a narrower ratio between medium and extractant compared with the 1:1.5 method. The standard values given in Table 13-11 also bear out this general relationship between test values obtained by the two methods. The 1:1.5 standard values are the guidelines commonly used by many of the testing laboratories in western European countries. These guidelines agree reasonably well with those developed by Verdure (1980) after 4 and 6 wk of plant growth. The SME standard values are used by many testing laboratories in the USA. Relative agreement between guidelines for the two methods is quite good, except for P.

Geraldson (1967, 1970) has shown nutrient balance in solution culture and in saturation extracts of weakly buffered sand soil to be of equal or greater importance than the quantities of nutrients present. He found a good nutrient balance as a percentage of total soluble salts to be: NO₃-N, 8 to 10; NH₄-N, <3; K, 11 to 13; Ca, 14 to 16; Mg, 4 to 6; Na, <10; and chloride, <10. Since most artificial growth media are weakly buffered, this nutrient balance logically applies for saturation extracts of these media. Expressing the nutrient contents as a percentage of total salts is helpful in as-

Table 13-12. Pour through soil solution elemental and soluble salt levels associated with vigorous growth of *Ilex crenata* and other nursery species growing in a pine bark medium (Wright, 1986).

Element	Concentration in leachate	
	mmol L ⁻¹	mg L ⁻¹
NO ₃ -N	5.3-7.1	(75-100)
P	0.32-0.48	(10-15)
K	0.77-1.28	(30-50)
Ca	0.25-0.37	(10-15)
Mg	0.42-0.62	(10-15)
Soluble salts	0.6-2.0 dS m ⁻¹	

sessing the most limiting nutrient or in the case of NH₄ and chloride, whether the potential for toxicity exists. Holcomb and White (1979) have shown that when plants are constantly fertilized through the watering system K is adequate at 3% of the total soluble salts. Recent studies by Biernbaum (1988, unpublished data) and George (1989) also indicate that top-quality plants can be grown with lower nutrient levels when subirrigation is used.

Nursery species that grow less rapidly than annual plant species have been shown to do well at lower media test levels. Table 13-12 presents the nutrient levels in a PT extract that Wright (1986) feels are adequate for good growth of a range of nursery stock. Nitrogen and P values agree with those in Table 13-11 and K falls in line as a percentage of total salts with the findings of Holcomb and White (1979). However, Ca and Mg values are much lower. Apparently, divalent cations do not reach the same equilibrium concentration in solution with the PT method as when media is mixed in the SME method.

Interpretation guidelines for the micronutrients are limited. Berghage et al. (1987) indicate that in 0.005 M DTPA saturation extracts B, Mn, Zn, and Fe concentrations of 0.065, 0.29, 0.21, and 0.27 mmol L⁻¹ (0.7, 16, 14, and 15 mg L⁻¹) respectively, may be near optimum. However, there was considerable variation in response to micronutrient levels in studies with mums, poinsettias, and marigolds (*Tagetes erecta* L.).

V. SUMMARY AND FUTURE CONSIDERATIONS

Unlike naturally occurring mineral soil, artificial growth media for producing containerized plants can be uniform across large geographical areas. Even though some growers continue to prepare their own special medium, the trend is toward uniform media prepared by large manufacturers. Uniformity of growth media cries out for a standard well-defined testing methodology that is applicable across large geographical areas. Currently, water extracts are the most popular with the 1:1.5 (Dutch) and 1:6 (v/v) methods being widely used in European countries. The SME method has received increased use in the USA. Variations of these methods such as the

PT method seem appropriate for special situations. The modified Spurway method continues to be used by some labs because they have a wealth of supportive data to aid in interpretation of results.

If the SME method is to receive strong support in the future, it will require generating an interpretative base for a large variety of plant types. A means will also need to be found for consistently mixing growth media to the point of saturation. Variation in judgment of the saturation point is currently the major weakness with the SME method.

Micronutrient testing of artificial growth media needs additional study. Regardless of test methodology, little information is available to assist in determining whether test values are low, optimum, or high. Recent developments with a DTPA modification of the SME procedure appears to have laid the groundwork for future progress in this area.

With increasing use of fairly uniform growth media, uniform reporting of results as well as establishment of uniform interpretation guidelines is essential. While nutrient concentrations in saturation extracts are acceptable indexes of nutrient availability, reporting soluble nutrient concentrations in a volume of growth medium may be more meaningful to growers.

Testing of artificial growth media has progressed significantly in the last 10 to 15 yr. To keep pace with developments in production management, continual research and refinement of testing methodology of growth media is essential for testing laboratories to service the greenhouse and nursery industries.

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Chapter 14

Principles and Practices in Plant Analysis¹

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The principles and practices of plant analysis have evolved over many years and changed as our scale of observation and depth of knowledge have improved. Early plant researchers identified the chemical elements found in plants. Initially, they concentrated on determining the elements essential for growth, development, and maturation of plants. An element is considered essential if a plant cannot complete its life cycle and produce viable seed for reproduction of the next generation without it. De Saussure (in France) conducted research on plant analysis at the earliest development level. The last element determined to be essential for plants in general was Cl (Broyer et al., 1954), which exists in the soil and plant as the chloride (Cl^-) ion. Field research has confirmed deficiencies of and responses to Cl^- in various parts of the world, including the Northern Great Plains and Pacific northwest in the USA (Jackson, 1986; Fixen, 1985; Fixen et al., 1986; Goos, 1986). In connection with Cl^- toxicities, crops such as corn (*Zea mays* L.) can essentially exclude it (Parker et al., 1985), while some varieties of soybean [*Glycine max* (L.) Merr.] are adversely affected by higher levels (Parker et al., 1983). Marschner (1986) has indicated that the discovery of the essentiality of other micronutrients ranged from Fe in 1860 to Mo in 1938. Cobalt was confirmed as an essential element for the symbiotic fixation of N in 1960 (Ahmed & Evans, 1960). Subsequent research has shown nickel (Ni) to be essential to that process (Dalton et al., 1985) and selenium (Se) to be beneficial (Evans, 1989).

Earlier reviews of the development of plant analysis have been written by Goodall and Gregory (1947) and Ulrich (1948). Chapman (1966) edited a comprehensive book that included use of plant analysis for diagnostic criteria for crops. Australian workers have published an interpretation manual on plant analysis (Reuter & Robinson, 1986).

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In terms of instrumentation for rapid analysis, it has evolved through the emission spectrograph, atomic absorption, x-ray fluorescence, mass spectrograph, electron microprobe, ion chromatograph, and the inductively coupled plasma (ICP) spectrograph. Near infrared reflectance instruments can be used to analyze some elements in forages, but lacks accuracy for others (Clark et al., 1987). Laboratories are now highly automated. Many elements can be determined simultaneously, on newer ICP instruments. The analytical instruments are linked to computers so that the results can be simultaneously printed for the researcher or customers' reports. These reports can either be mailed to the customer or sent electronically for more rapid transmission of results. The latter are printed out on site for further analysis and interpretation.

Plant analysis in a narrow sense is the determination of the elemental composition of plants or a portion of the plant for elements essential for growth. The concentration or extractable fraction of an element is determined from a sample taken at a specific time or stage of physiological or morphological development. The concentration is usually expressed on a dry matter basis. In a broader sense, plant analysis could include determination of specific organic compounds or substances such as amino or organic acids, plant growth substances, or hormones. It can also include determining elements that are detrimental to growth or animals and humans through our food chain. In this chapter, we deal with plant analysis in its narrower sense.

Plant analysis has become an integral part of most agronomic experimentation and is used to document and verify treatment effects. It is also used at the farm level by dealers and crop consultants to monitor production fields. Many private and public laboratories extend their services to dealers and farmers alike, and field use has greatly increased to confirm deficiency symptoms, diagnose problems, and search for the critical path to improved yields and profitability in crop production. This chapter covers the basic principles and relationships involved in plant analysis.

I. BASIC PRINCIPLES

Plant analysis is based on the principle that the concentration of an element or nutrient within the plant or one of its parts is an integral value of all of the factors that have interacted to affect plant growth, including the availability of the element. From an essential element standpoint, other than C, O, and H, which are derived from the air and soil water, we are dealing primarily with N, P, K, Ca, Mg, S, B, Cl, Cu, Fe, Mn, Mo, and Zn for most crops, with the addition of Co and Ni for symbiotic N₂ fixing bacteria associated with legumes. Sodium and Si have been shown to be essential for some crops, while in other cases they have been highly beneficial and provided economic crop responses. For example, in studies on wild rice (*Oryza sativa* L.) yield increases of nearly 50% have been found in response to Si application (Bloom & Meyer, 1988).

Much research has involved determining the optimum concentration of essential and beneficial elements for a given crop under experimental conditions. Realistically, under the usual two-dimensional experimentation, yield vs. one nutrient variable, seldom are all of the elements at or near optimum levels. If one element is found limiting, the sufficiency of others cannot really be determined until the limiting element is brought to sufficiency. Also, other nonessential elements, such as Al, above specific concentrations can adversely affect root and shoot growth, influencing the availability and uptake of other elements, and yields (Ohki, 1987). Excess concentrations of essential elements can also become detrimental to growth and lead to yield decreases.

The steps in plant analysis involve: (i) Collecting a representative sample or a portion of the crop, sampled at a time or stage of development that will be useful in reflecting its true nutrient status. (ii) Handling the sample so that the analysis will provide an accurate measure of the crop's elemental status. (iii) Using the best method and instrumentation for chemically analyzing the elements of interest or their fractions. (iv) Having enough knowledge so that the results of the analyses can be properly interpreted from a research or advisory standpoint. (v) Making recommendations to economically improve the nutrient status and productivity of the crop.

Steenbjerg (1951) discussed various yield curves and the relationships that are found with plant analysis. In the following sections, basic principles and specific examples of some relationships will be shown.

A. Yield in Relation to Nutrient Concentration and Supply

In developing the basic relationships among or between growth rate, dry matter accumulation (yield) and nutrient supply or concentration in the crop, usually one, two, or at most three elements are varied in an experiment. All others are considered to be present in the adequate amounts range. It should be remembered that when one element is added in increasing amounts, one or more other elements are usually being applied at the same time. Therefore, systems are seldom as well controlled as we would like in most studies.

A typical model or curve of relationships involving crop yield and nutrient concentration with increasing nutrient supply from the soil and fertilizer is shown in Fig. 14-1. Nutrients other than the one being considered are assumed to be in adequate supply. If one were to view the entire yield curve on a soil essentially devoid of the limiting element, the curve would be sigmoid with increasing nutrient supply. In field experiments, usually only segments of continuous curves are found in a given year due to the varying levels of the limiting nutrient in or released by the soil. The concept and segments of the curves as presented are similar to those Macy (1936) proposed. The concept as presented does not consider economics, but indicates interrelationships. Also, remember that curves or regressions are estimated with error. Therefore, the points on the curves, such as optimum yield, critical percentage, critical level, or optimum are estimated with associated errors, which indicates ranges rather than specific values.

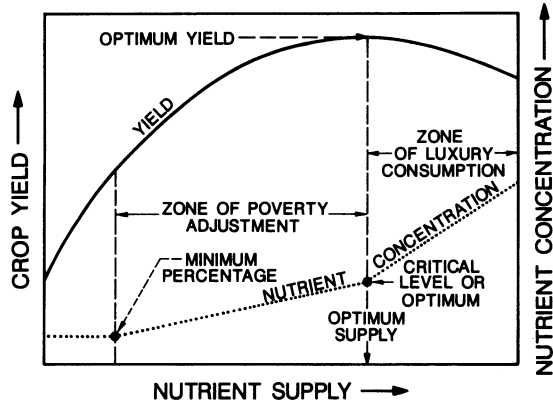


Fig. 14-1. Schematic graph of the manner in which nutrient concentration and crop yield varies with the supply of nutrient (Brown, 1970).

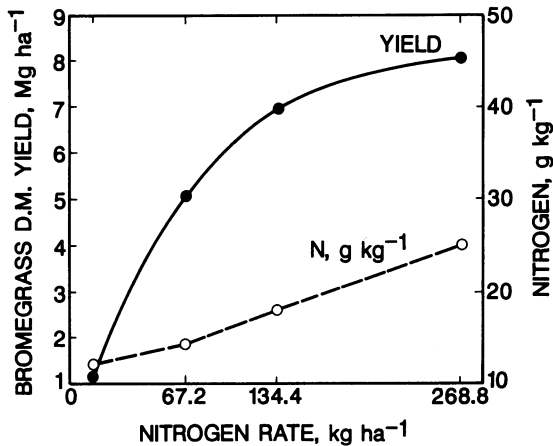


Fig. 14-2. Yield of first cutting of bromegrass and its N concentration as related to N applied as ammonium nitrate (Russell et al., 1954).

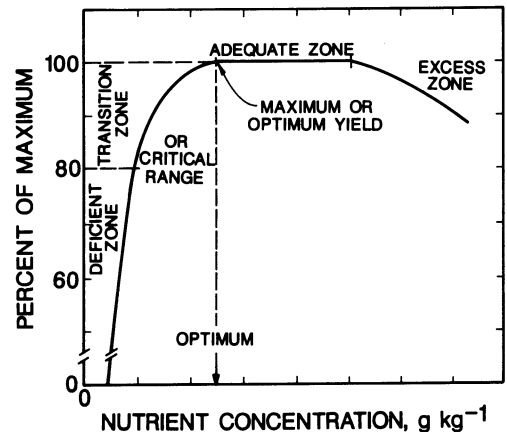


Fig. 14-3. Schematic showing the relationship between percentage of maximum yield of growth rate and nutrient concentration of a specific plant part sampled at a given stage of development (Ulrich & Hills, 1967; Dow & Roberts, 1982).

Results from a field study in which N rates were applied to a single cutting of smooth brome grass (*Bromis inermis* Leyss.) are shown in Fig. 14-2. It appears that the plant analysis range includes the minimum percentage and zone of poverty adjustment, approaching the critical N concentration that produced the highest or optimum yield. The objective of evaluating results of such studies is to determine the critical or optimum concentration so that plant analysis can be used to monitor the sufficiency of the nutrient in terms of need or supply. Unfortunately, the zone of luxury consumption or concentration could not be evaluated from this example.

B. Yield or Growth Relationships with Nutrient Concentration

Graphing the yield and nutrient concentration is the approach often used to determine the critical level or concentration of an element in a given crop. Ulrich (1949, 1961, 1976) and his colleagues (Ulrich & Hills, 1967), as well as others, (Ohki, 1976, 1984a, b) have used this technique for many crops and found it particularly useful. The technique is based on the fact that if a plant is deficient in an element, growth rates and yields will be decreased. By adding increasing amounts of the nutrient applied, the concentration of the element in the plant or plant part increases until an optimum level is reached. Growth or yield using this approach is expressed as a percentage of the maximum. A schematic of this type of relationship for an element is shown in Fig. 14-3. Note how rapidly growth or yield declines when concentrations are in the deficient zone or range.

The zone between the deficient and optimum concentration in Ulrich's approach is referred to as the *transition zone*. Ulrich indicated that the transition zone starts with concentrations that produce about a 20% reduction in growth or yield and continues to those that produce the optimum or 100% of the maximum. Dow and Roberts (1982) have referred to this zone as the *critical range* within which the researcher may select the yield reduction and nutrient concentration considered acceptable. Ulrich and his colleagues set the critical level at concentration that produced a 10% reduction in growth or yield. Ware et al. (1982) found that it made a great deal of difference in the critical level determined, depending upon if a graphic analysis or a Mitscherlich model were used. Usually the concentrations determined by the Mitscherlich model were significantly greater than those determined by graph analysis.

In general, the yield reduction that a researcher is willing to accept in setting the critical concentration is subjective and could depend upon several factors. These factors include the sophistication of the production system, economic value of the crop, environmental constraints, and the risk and uncertainty associated with the system. Parker and Walker (1986) in connection with peanut (*Arachis hypogaea* L.) production and Mn concentrations concluded that "if concentrations of Mn in peanut leaves is only high enough to produce 90% of maximum yield and corrective treatments are not made, growers can suffer severe economic losses because peanut is a high

income field crop.” The same could be said for many other crops and production systems if economic considerations alone were the only consideration. Roberts and Dow (1982) have suggested critical range values that produce 95 to 100% of maximum yield for irrigated potato (*Solanum tuberosum* L.), a high value crop. They refer to concentrations above those necessary for maximum yield as adequate, which would correspond to the sufficiency range or optimum range used by others (Planck, 1979; Embleton et al., 1976). In our example in Fig. 14-3, the optimum was selected as being that associated with the maximum yield. However, under a high-risk production system, such as tropical pastures, a researcher might accept a critical concentration as associated with 80% of maximum yield (Lanyon & Smith, 1985).

The reason we have accepted the optimum concentration or yield at 100% of maximum relates to the percentage sufficiency concept and nutrient interactions. Based on the percentage sufficiency concept, if two essential elements were at concentrations in the plant that would only allow a yield of 90% for each element, all others being at the optimum or 100%, the highest rate of growth or yield that could be achieved would be 81% of maximum ($0.9 \times 0.9 = 0.81 \times 100 = 81\%$). Assuming that there are 13 mineral elements that come from the soil and one accepts a critical concentration for each at a level that will produce a yield that is 90% of maximum, theoretically using 0.9 multiplied by itself 12 times for the 13 elements, the highest yield that could be achieved would be just over 25% of the maximum potential. Even if all elements were at concentrations that would produce 95% of maximum, based on the concept, one could only achieve 51% of the potential yield level. It is our view that the validity of this concept has not yet been adequately tested or verified, in spite of some practical evidence that would support it.

Hylton et al. (1967) have shown that the critical level of one element can shift rather widely if another element can substitute or interfere with the uptake of the first element. For example, with Italian ryegrass, they found that the critical level for K increased from 8 to 35 g/kg (0.8–3.5%), depending on the concentration of Na in the blade tissue. Ulrich and Hills (1967) and Hills and Ulrich (1976) point out the importance of this interrelationship for sugarbeet (*Beta vulgaris* L.). Sodium concentration influenced the range of K concentrations at which leaf petioles or blades show deficiency symptoms. Reneau et al. (1983) discussed the interrelationships between yield, K, and Mg concentrations in forage sorghum [*Sorghum bicolor* (L.) Moench] with P and K fertilization. Munson (1968) discussed the interrelationship of cations in plants and the manner in which nutrient additions, nutrient sources, and several other factors can influence yields and nutrient concentrations.

The adequate zone in Fig. 14-3 conforms to the sufficiency zone or optimum range terms used by others. It is a range that indicates nutrient concentrations that are at or above those needed for maximum yields under the conditions of the experiment, but with no reduction in yield. Some might refer to concentrations above the optimum levels as an indication of luxury consumption, while others would only indicate adequacy or sufficiency as

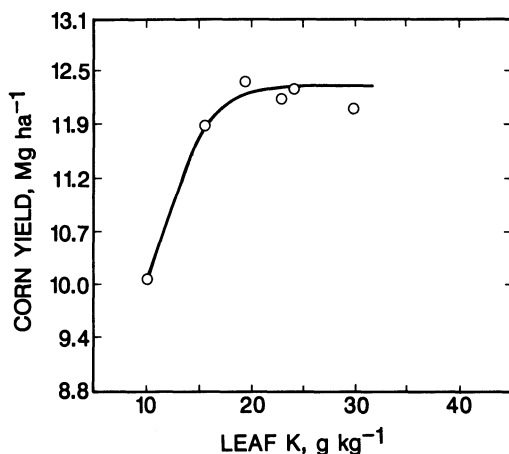


Fig. 14-4. Relationship of corn yield to leaf K concentrations sampled at tasselling stage of development (Overdahl & O'Leary, 1981).

long as yields were not reduced. When concentrations of one element increase above adequacy, one always needs to evaluate other elements to determine if they indeed might be limiting or are present in excess. When yields are decreased by higher concentrations of one nutrient, the level would be in the excess zone or at a level some would refer to as toxicity or excessive.

The relationship between irrigated corn yield and leaf K concentrations sampled at tassel is shown in Fig. 14-4. As K concentrations of leaf K were increased from 10.5 to 19.3 g/kg, grain yields were increased 2320 kg/ha (37 bu/acre), reaching a yield of 12.4 Mg/ha (198 bu/acre). No further increase in yield was observed, even though leaf K concentrations were increased to nearly 30 g/kg. This may indicate the possibility of other limiting elements or production constraints. With irrigation the minerals in some coarse-textured soils, such as those used in this study, release significant amounts of K, even though the K soil test is relatively low. However, these soils will not produce optimum yields unless additional K is applied (Overdahl & O'Leary, 1981), even with irrigation.

Chapman (1967) presented a yield-nutrient concentration relationship curve. A modification of that curve and the terminology is shown in Fig. 14-5. Note that the deficiency range is divided into severe and low and the optimum yield and optimum concentration are associated with the beginning of the sufficiency range. The lower portion of the curve may be found with an element such as a micronutrient, when the initial deficiency is severe and increased availability greatly increases dry matter yields, causing a dilution of its measured concentration.

In actual practice, it is of little value to sample a crop with different treatments for comparative purposes until plants have developed sufficiently to cause differential concentrations among the treatments. Data of Viets et al. (1954) indicate that the N concentrations in corn leaves sampled 17

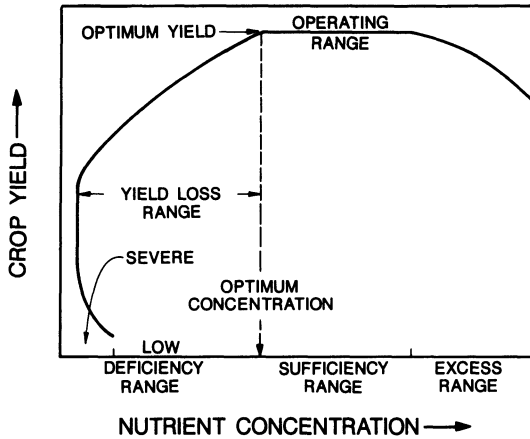


Fig. 14-5. Schematic of yield or growth of a crop as related to nutrient concentrations with interpretive ranges (Chapman, 1967).

June did not differ over N treatments, since all were at or above the critical level (Fig. 14-6). However, samples taken 9 July were sufficiently different in concentrations so that a meaningful relationship could be determined. With that sampling it appeared that even the highest N concentration was below that necessary for the optimum yield. Because of experiences such as these, sampling at a specific stage of development is usually suggested. For example, for corn leaf samples, it is recommended that the ear leaf or the leaf opposite and below the ear is sampled when the crop is 75% silked or entering the reproductive development stage.

Loué (1963) found the relationship between corn grain yield and leaf K shown in Fig. 14-7. He suggested that rather than referring to a specific critical level, it would be better to refer to a critical zone, which he determined to be between 17 and 20 g/kg (1.7 and 2.0%) K. It is presumed that if the level fell below 17 g/kg, the sample would be deficient.

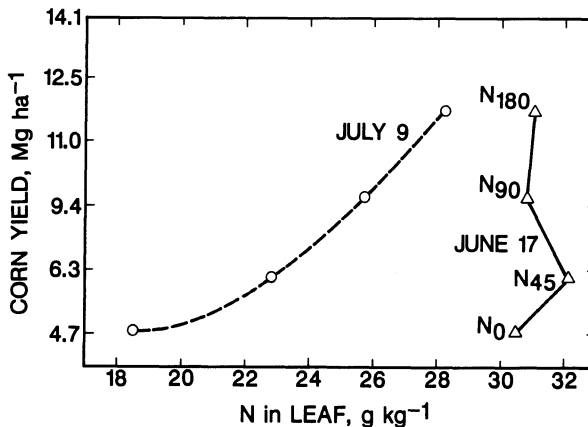


Fig. 14-6. The relationship of corn grain yield and leaf N composition as influenced by rates of N and date of sampling (Viets et al., 1954).

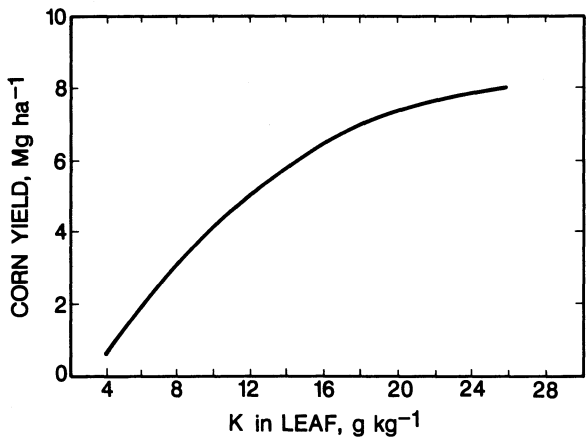


Fig. 14-7. The relationship of corn grain yield and K composition of the ear leaf sampled at silking (Loué, 1963).

Rehm et al. (1983) have conducted P studies on corn. They used regression analysis relating the percentage of maximum yield of silage or grain to either ear leaf P or P concentration in whole plants at maturity. Using the respective quadratic regression equations and solving for optimum ear leaf P concentration for maximum yield, the optimum levels were found to be 2.63 g of P/kg for silage and 2.64 g of P/kg for grain. When whole plant analysis were used, the optimum P concentrations were 2.85 g/kg for silage production and 3.46 g/kg for grain production. They noted substantial year-to-year variations in the affects of applied P on leaf P and in the mature crop.

Because in field situations one seldom deals with one element at a time and percentage of maximum yield is the criterion used to determine the optimum concentration, it could be beneficial to evaluate the leaf concentrations of essential nutrients found in corn from experiments that approach current maximum yields. Roy L. Flannery (1987, personal communication) of the New Jersey Agricultural Experiment Station provided the plant analyses of corn leaves sampled at early tassel from five experiments conducted on the same experimental site for 5 yr, with grain yields ranging from 17.9 to 21.2 Mg/ha (Table 14-1). It is assumed that these values are within the

Table 14-1. Corn yields and elemental ear leaf concentrations sampled at early tassel for 5 yr. (R. Flannery, 1987, personal communication).

Grain Percent yield max.		Elemental concentration-ear leaf									
		N	P	K	Ca	Mg	S	Mn	Zn	Cu	B
Mg/ha		g/kg						mg/kg			
21.2	100	33.8	3.2	23.9	5.9	1.8	2.8	41	28	10	21
19.6	92	31.8	4.0	22.8	5.3	1.5	2.0	43	39	11	14
19.4	91	31.6	4.1	26.1	4.8	1.8	1.9	39	26	9	7
18.1	86	30.4	3.4	26.6	6.1	1.9	2.3	37	28	12	12
17.9	84	30.2	3.2	26.3	5.8	1.8	2.2	36	27	10	10
Mean values											
19.2		31.4	3.6	25.1	5.6	1.8	2.2	39	30	10	13

sufficiency range for each element because of the high yields achieved. Walworth et al. (1988) have used these values in developing DRIS norms, which will be discussed in a later section of this chapter.

Flannery (1982) provided the analyses of trifoliolate soybean leaves sampled at early flowering for soybean that yielded 7.3 Mg/ha (113 bu/acre). This yield approaches current experimental maxima for soybean. The results were as follows: N, 58.2 g/kg; P, 4.3 g/kg; K, 22.3 g/kg; Ca, 9.1 g/kg; Mg, 3.2 g/kg; S, 2.4 g/kg; B, 42 mg/kg; Cu, 12 mg/kg; Fe, 126 mg/kg; Mn, 35 mg/kg; and Zn, 50 mg/kg. These values should be within the sufficiency range for the elements determined.

C. Nutrient Concentrations and Physiological Maturity

In establishing sampling procedures for plant analysis, the researcher and user must be aware that the concentrations of elements or soluble fractions change rather rapidly with time and physiological maturity. The major reason for this is rapid dry matter accumulation and dilution of the nutrient concentrations, even though the uptake of some nutrients continue until near maturity. Tyler and Lorenz (1962) have shown that potato petiole nitrate-N ($\text{NO}_3\text{-N}$) and phosphate-P ($\text{PO}_4\text{-P}$) increase with rates of application and decrease with seasonal sampling and development stage. From such information, one can extend the seasonal sampling period and determine whether the level of nutrition of a given field is in the sufficient, intermediate, or deficient ranges.

Dow and Roberts (1982) have proposed and Roberts and Dow (1982) have discussed an approach using seasonal critical nutrient range (CNR). In potato rate of P studies on two soil types, yields and petiole samples were taken for each P rate at five sampling dates during the growing season. From these data, Dow and Roberts regressed percentage petiole-P on sampling dates in days after formation of 2-cm tubers to determine two regression equations which encompassed yields between 95 and 100% of maximum. These equations were used to establish the seasonal P deficient, CNR, and adequate P levels (Fig. 14-8). Early in the season, the CNR for petiole-P was from 3.8 to 4.5 g/kg (0.38–0.45% P), while for the last sampling the range was from 1.4 to 1.7 g/kg.

Lutrick et al. (1986) used a graphic analysis to monitor seasonal NO_3 levels in cotton (*Gossypium hirsutum* L.), breaking the ranges into deficient, adequate, and excess. Either approach should be applicable for any nutrient or combination of nutrients, to determine adequacy anytime during the growing season. The critical range should provide a more certain guide than that used by Westermann and Kleinkopf (1985a), which sets a level of total P concentration in the tops and active leaves of potato at >2.2 g/kg as being adequate for dry matter production and tuber growth rate. Westermann and Kleinkopf (1985b) used a similar approach for N and concluded that a fourth petiole $\text{NO}_3\text{-N}$ concentration of 15 000 mg/kg was a concentration adequate for optimum dry matter production.

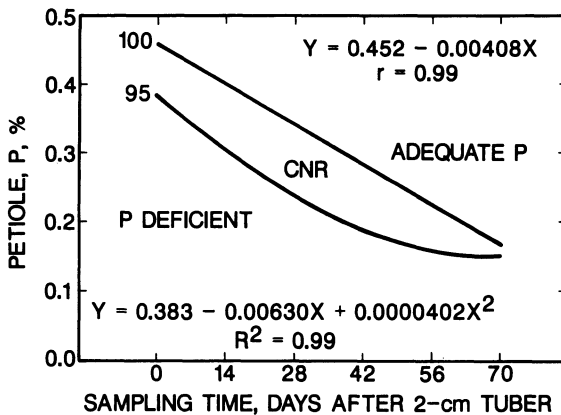


Fig. 14-8. Use of 95 and 100% of maximum potato yield regression equations to establish seasonal petiole P deficient, critical nutrient range, and adequate P levels sampled after 2-cm tuber formation (Roberts & Dow, 1982).

Many researchers have studied the changes in nutrient concentrations of different plant parts of crops over the growing season, but few have used modeling or regression techniques, such as applied by Roberts and Dow (1982). The latter approach is sound if elemental concentrations are increasing or decreasing. Sayer (1955) conducted extensive research on concentrations of elements in various portions of corn inbreds and hybrids at different stages of maturity. More recent research on a given hybrid was conducted in Iowa under low and higher fertility levels with respect to P and K based on the research of Nael El-Hout (R. Killorn & R.D. Voss, 1985, personal communication). Leaves, sheaths, stalk, tassel, lower leaves, husks, shank, silks, cobs, and grain were analyzed from developmental stage V4 to R1 and every 11 d after that for 55 days. The concentrations of each portion was determined for each sampling date, as well as to total amounts of N, P, K, S, Ca, and Mg in each portion and the total crop. These are probably the most thorough set of data that exist for an intermediate yield level of 10.16 Mg/ha. Others have analyzed portions of corn plants samples at different times over the season, including Hanway (1962), Gorsline et al. (1965), Flannery (1986a), and Karlen et al. (1988). Using the dry matter and amounts of nutrients in the aerial portion of the crop, calculations from Flannery's research indicates the following changes in concentrations for nutrients at 32 d after emergence to Day 146: N, 42.6 to 12.2 g/kg; P, 4.64 to 2.16 g/kg; K, 55.9 to 11.0 g/kg; Ca, 3.55 to 1.87 g/kg; Mg, 3.55 to 1.38 g/kg; and S, 2.13 to 1.27 g/kg.

Grain

Some researchers have used postharvest analysis of grain as a means to determine whether a crop was grown under optimum levels of nutrition. Pierre et al. (1977a, b) studied the relationship between the N concentration of the corn grain and yield expressed as a percentage of maximum as a meas-

ure of N sufficiency. They used both regression and graphic techniques. They found that when corn yields approached maximum yields based on N-fertility studies, the postharvest N concentration of the grain was 15.2 g/kg by graphic analysis or 15.4 g/kg based on regression analysis. These concentrations would be viewed as the critical levels at which N would not have been the limiting factor to yield. It does not guarantee that some other nutrient or management practice might not have been limiting. They used this technique to estimate a N requirement index (NRI) need for different situations to increase yields to either the maximum or economic optimum. Based on their analysis, it would take an average of 34 kg of N to produce a megagram of grain when yields were 45% of maximum, but about 75 kg of N when yields were at 90% of maximum.

Randall et al. (1987) studied increasing rates of N using two commercial adapted corn hybrids where the previous crop was corn or soybean. The N concentrations of the grain for the two hybrids were different even though yield increases from additional N were small or negligible. One hybrid following corn yielding at 99.6% of maximum had a N grain concentration of 11.8 g/kg. Following soybean with corn yields of 97 and 98% of maximum, the two hybrids had grain N concentrations of 12.3 and 13.6 g/kg, well below the levels suggested by Pierre and his colleagues. Following soybean, the yields of the two hybrids were 1.38 and 1.59 Mg/ha greater than following corn.

Ray Lockman (1986, personal communication) has analyzed field samples of corn grain taken from an Illinois farmer's (Herman Warsaw) test area that had yielded 20.446 Mg/ha (326 bu/acre) or 17.28 Mg/ha of dry matter. That yield approaches current maximum yields being grown. On a dry matter basis, the nutrient concentrations of the grain were as follows: N, 16 g/kg; P, 3.4 g/kg; K, 3.7 g/kg; Ca, 0.4 g/kg; Mg, 1.1 g/kg; S, 1.3 g/kg; Cu, 3.8 mg/kg; Fe, 34 mg/kg; Mn, 8.9 mg/kg; and Zn, 30 mg/kg. From these values, using the dry matter yield of the grain, one can estimate the amounts of nutrients removed from the field.

Dumenil (1974), working on soil productivity in Iowa, related P and K concentrations in the grain of corn, oat, and soybean to increasing soil test values. With P, as the soil test values were increased from 5 to 50 mg of P/kg, the P concentration of corn grain increased from 1.9 to 3.6 g/kg, oat from 2.5 to 4.5 g/kg, and soybean from 4.5 to 7.3 g/kg. With increasing soil K levels from 25 to 350 mg of K/kg, the K concentration of corn grain increased from 3.0 to 5.1 g/kg and soybean increased from 16.9 to 25.3 g/kg. No attempt was made to relate the concentrations to the yields in these studies. However, it should be noted that Sale and Campbell (1986) found that the yield of soybean and oil ($r = 0.97$), protein ($r = -0.94$), and K concentration ($r = 0.98$) were closely related. Bean yields increased until the K concentration of the mature beans was > 18 g/kg. Results from field studies in which yields were from over 4.4 and 5.8 Mg/ha, the K concentrations of the bean of soybean were 18 and 17.9 g/kg, respectively (see Table 2, Bundy & Oplinger, 1984). Goos et al. (1982) used grain protein of winter wheat as a postharvest measure of N sufficiency for maximum yield of grain. They

determined the critical grain protein level to be 115 g/kg and determined that the transitional zone between deficient and sufficiency ranged from 111 to 120 g/kg.

D. Nutrient Concentrations and Variety or Hybrid

Many researchers have observed that genetics exerts a high degree of control over nutrient uptake and concentrations in plants, the actual concentration reflecting genetics, cultural practices, and environmental conditions. Genetics establishes the boundaries of physiological and metabolic potential. Manipulation of cultural and management practices, nutritional regime, and environmental modification determines to what extent the genetic potential is fulfilled. Munson (1970, 1974) has reviewed genetics and nutrient concentrations for many crops. Munson and Nelson (1973) included a section on the subject. Parks (1985) has specifically evaluated K variability with varieties and hybrids for many crops. Carlone and Russell's (1987) evaluation of 28 corn genotypes developed and used during different eras in corn production have found marked differences in their response to plant densities and N rates. While N concentrations were not studied per se, this represents a classic paper for those interested in genotypes and interactions with nutrient response.

Some of the differences among varieties or hybrids relate the differential capacities of roots to absorb or take up nutrients. Baligar and Barber (1979) found that four parental corn genotypes from Indiana and four from Florida and their single crosses exhibited different appearing root systems, causing differential rates of nutrient uptake in short-term studies. The single crosses exhibited heterosis in growth of shoots and roots. The ranges in I_{\max} values among the Florida genotypes were much greater for K, Ca, Mg, and P in terms of $\mu\text{mol (cm/s)}$, the values being 0.75 to 2.96, 0.32 to 1.08, 0.04 to 0.28, and 0.18 to 0.89, respectively, than for the Indiana genotypes. The latter genotypes showed ranges of 1.30 to 2.06, 0.04 to 0.23, 0.12 to 0.19, and 0.09 to 0.19 for the same elements.

Elliott and Lauchli (1985), in studying 15 different corn inbreds, found significant differences among genotypes for rates of P utilization, but not for P absorption by roots. The lack of P use was thought to be limited by partitioning of P between free orthophosphate and that organically combined. However, in these studies, all genotypes exhibited a P-induced Fe deficiency caused by an apparent inhibition of Fe transport from the roots to the shoots. This brings up the direct and indirect effects of applying an increasing rate of a nutrient or nutrients to soils and the resultant impact on the availability of nutrients other than those being applied.

Bruetsch and Estes (1976) evaluated 12 corn genotypes of differing relative maturities, with final yields ranging from 10.9 to 14.3 Mg/ha, for variations in dry matter, and nutrient accumulation. They found that there was significant variability among genotypes with respect to dry matter and nutrient accumulation. Nutrients that showed genotype differences in dry weight production per gram of nutrient were N, P, K, Ca, and Mg. The rela-

tionship between P concentration and relative maturity of the genotype was most consistent, with the higher P concentrations being in the earlier maturing genotypes. However, in terms of efficiency of dry matter produced per unit of P absorbed, the later-maturing hybrids ranked highest.

Malzer et al. (1984) under high yield conditions evaluated nine different corn hybrids for grain yield, leaf nutrients, grain and stover nutrients and total uptake. In most cases, the results indicated a high probability of differences among the hybrids for the criteria measured. Different hybrids also appeared to respond differently depending upon the previous crop (corn after corn or corn after soybean).

Mackay and Barber (1986) studied the N uptake and root growth in response to N to explain the differences between two corn genotypes, Pioneer 3732 and B73 \times Mo17, on two soil types. They found that in contrast with the P 3732 hybrid, by midsilk, N increased the root length of B73 \times Mo17 on both soils by 35 and 37% and showed extended root growth after midsilk. They proposed root growth after midsilk as one mechanism to explain the advantage of that hybrid under higher N rates. They did not evaluate the effects of N on the leaf concentrations or uptake of other elements.

Ebelhar et al. (1987) studied the response of prolific (Pr), semiprolific (SPr) and nonprolific (NPr) corn genotypes to N and K rates at two plant populations. They found that increasing N rates resulted in greater K uptake and that N rate in fact had a greater effect on K uptake than K rate. This caused differential leaf concentrations of Ca, Mg, and K among the genotypes. The Pr and SPr genotypes showed greater increases of Ca, Mg, and K in response to N rates than did the NPr genotype. There was a marked genotype effect of K rate on K uptake with the Pr and SPr lines taking up more K than the NPr line. Maximum yields were obtained with leaf N concentrations of 28 to 30 g/kg for yields that ranged from 12.1 to 13.6 Mg/ha, depending upon the year. Increased N concentrations increased Ca + Mg/K ratios for the Pr genotype, but did not change those of the NPr. Earlier, Anderson et al. (1984) studied the effects of N on several factors related to the prolificacy of genotypes and found differences among the lines with respect to N concentrations in grain, with the NPr being the highest, 15.7 to 16.0 g/kg, and the Pr being the lowest, 12.6 to 13.7 g/kg.

Differences in nutrient concentrations between and within species and cultivars have been studied by many. Some of these include studies on corn by Baker et al. (1970) and Gallaher et al. (1972); forage legumes by Loper and Smith (1961); soybean by Karlen et al. (1982), Gettier et al. (1985), Sale and Campbell (1986, 1987), and Silberbush and Barber (1985); barley (*Hordeum vulgare* L.) by Dick et al. (1985); tomato (*Lycopersicon esculentum* Mill.) by Carpena et al. (1988); cotton by Anderson and Harrison (1970); and peanut by Coffelt and Hallock (1986).

E. Interrelationships with Other Factors

Availability of an element has a dominant effect on the concentration of that element found in a plant or plant part being analyzed, but it can also

have a dominant effect on the uptake and concentration of one or more other elements. An earlier example was given for N and K, as well as for the relationships between K and Na in some species. If a nutrient such as N is applied and the availability of another essential element is limiting, initially, there may be a decrease in the concentration of the limiting element, and its concentration will drop to the minimum necessary to support growth. By the same token, because of the effects of soil moisture (Mackay & Barber, 1985a, b; Kuchenbuch et al., 1986) and temperature (Kuchenbuch & Barber, 1988) on nutrient availability and uptake, they can exert influences on the concentration of elements in plant tissue. The drought of 1988, for example, produced K deficiency symptoms on soils that under more normal soil moisture would not have shown apparent symptoms. Diagnosticians need to be aware of the differences within a season and among seasons even at the same experimental site. These differences may complicate interpretation unless adequate ranges are used. Changes in management practices such as increasing plant densities per unit area, changing tillage or increasing soil compaction, or adjusting soil pH may cause nutrient concentrations to change depending upon their effects upon nutrient availabilities.

F. Nutrient Use Efficiencies

A researcher can determine how efficiently a crop is using a nutrient internally by measuring the total uptake of the nutrient and determining how much yield, either dry matter or harvested portion, is produced per unit of nutrient. This requires total dry matter measurements and plant analysis. These values will not indicate how efficient a particular crop is in recovering either soil or fertilizer nutrients unless other comparisons are made. For corn, which produced 2-yr-average-yield over 20 Mg/ha, R.L. Flannery (1985, personal communication) found that average grain output/uptake ratio based on total aerial or aboveground uptake were 48.8 kg of grain/kg of N, 240.8 kg of grain/kg of P, 50.6 kg grain/kg of K. Rhoads and Stanley (1981) found grain output to uptake ratios of 62.2 for N, 295 for P, and 50.8 for K for corn that yielded 12.7 Mg/ha. For corn yields of 13.5 Mg/ha, Karlen and Camp (1985) found grain to uptake efficiencies of 59.4 kg of grain/kg of N, 221 kg of grain/kg of P, and 50.7 kg of grain/kg of K. The efficiencies for P among the three studies varied the most, but those for K were amazingly similar. The standard deviations for this small sample were 38.3 for P, 7.68 for N, and 0.1 for K. It is easy to take the reciprocal of the above efficiency values, multiply them by 1000 and obtain estimates of the total uptake per metric ton of grain production.

For soybean that produced 6787 kg/ha, Flannery (1986b) found that for the output per unit of highest seasonal nutrient uptake, efficiencies were 11.05 kg of bean/kg of N, 105.1 kg of bean/kg of P, 16.86 kg of bean/kg of K, 36.78 kg of bean/kg of Ca, 107.7 kg of bean/kg of Mg, and 218.9 kg of bean/kg of S. The above values and those for corn provide an indication of the internal efficiency with which these crops convert nutrients taken up into grain yield under high-yield conditions. From an energy standpoint,

the relationship found between corn and soybean produced per unit of K uptakes K is interesting. Usually it is considered to take three times the energy to produce a unit of soybean as a unit of corn, because of the greater oil and protein contents of bean. If one divides the mean output per internal unit of input of K for corn from the above example (50.7 kg of grain/kg of K) by three, you obtain 16.9 kg of grain/kg of K, which is the same value found for soybean (16.86 kg of beans/kg of K). This may indicate the nutritional importance and stability of K in energy relations in both crops.

The recovery of one nutrient from the soil or a fertilizer application depends upon the availability of a second nutrient. For example, K uptake and efficiency from either soil or K applications often depend upon the rate of N used (Ebelhar et al. 1987). Likewise, if K availability or supply is low, N uptake and utilization may be very low. Similar interrelationships are observed between N and P. In the Iowa studies of Nael El-Hout, mentioned earlier, increased application of P and K, with the same rate of N, increased yield by 74% (5.7–9.93 Mg/ha); N uptake by 68%; P uptake by 253%; K uptake by 162%; S uptake by 39%; Ca uptake by 46%; and Mg uptake by 20%. It may well be that nutrients other than P and K became limiting at higher rates of these nutrients. With the environmental issues that confront us, there will be increased emphasis on the efficiency of nutrient recovery and more stress will be placed on determining limiting factors, and on varieties or hybrids that increase the output per unit of soil or applied nutrient. It is unlikely that simply looking at leaf concentrations will produce the answers needed for the future. Plant analysis can, however, be used to monitor crops throughout the growing season for nutrient adequacy.

II. PRACTICES OF PLANT ANALYSIS

Research has established critical or optimal levels of nutrients for crops, as well as levels considered to be deficient, low, sufficient, or excess. These will be discussed in detail for the various crops in subsequent chapters. It is interesting that variations in these values exist among states and experiment stations. Perhaps this is not surprising when one considers the weather, climate, and soil differences, as well as genetic differences in specific crops that exist. In each case, one assumes that data were properly evaluated in determining the established values. Optimal values will stand the test of time and experimentation and practical use in the field by practicing agronomists, soil scientists, and crop consultants.

The availability of plant analysis facilities has increased markedly. Most land grant universities have laboratories that are used in both research and extension and are available to farmers and dealers for a fee. Also, many private laboratories have agronomists or crop consultants that work directly with dealers to serve their customers.

A. Experimental Techniques

Every year many soil fertility experiments are conducted in which the nutrient availability is varied, both in terms of nutrient soil test levels and fertilizer application. Plants are sampled and analyzed at appropriate times to relate these values to growth and yield. These are used to improve our knowledge base through calibration and correlation studies. If and when enough new data become available, researchers may adjust the critical or optima levels or ranges that are currently being used. With such input, there is a continual shifting and updating of information based on the latest results that may come with newer varieties or hybrids and cultural or management practices. The trend to analyze for all of the essential elements, as well as for heavy metals or those that may cause health and nutritional problems broadens the usefulness of the information collected.

B. Verification of Specific Symptoms

Nearly every crop consultant or practicing agronomist has used plant analysis to verify the adequate nutritional status of crops or identify an apparent nutrient deficiency. While nutrient deficiencies should be rare in high production systems, nevertheless, they are observed from time to time. If young plants are sampled and deficiencies found, often there is still time to make corrective applications of nutrients, heading off the possibility of large economic losses. Sometimes the apparent symptoms of an excess of one element will look like the deficiency of another element. For example, excess B in corn produces symptoms that appear similar to K deficiency. Plant analysis provides direction for proper action.

C. Field Surveys

Field plant analysis surveys are used by researchers, and extension and industry personnel to provide information about possible deficiency of a specific element or elements and to define the area over which the deficiency exists. Such surveys usually involve an indicator crop, which may be particularly sensitive or has a high requirement for the element in question. Some industry people have used this technique within a given trade area and may refer to it as a 'Blitz'. Both soil sampling and testing are combined with the plant sampling and analyses for complimentary information. Researchers in many states have also used these techniques to define the boundaries or soil associations in which specific problems exist. Lanyon and Griffith (1988) cite data, for example, showing that the ratios of K fertilizer applied to K removals for alfalfa (*Medicago sativa* L.) and corn grain in the USA are 0.28 and 2.8, respectively. Such discrepancies need to be carefully studied to evaluate soil test levels, the capacities of the two crops to recover and respond to soil and fertilizer K, and the amounts needed for increases or maintenance of yield.

D. Analyses of Normal and Abnormal Plants

Sometimes no apparent deficiency symptom is showing in plants, but a comparison of different portions of a field make it obvious that some areas are not growing normally. In such situations, it is helpful to be careful in your evaluation. It is important to dig up plants and examine roots, look for insect feeding, nematode damage, or disease symptoms, as well as examining the soil for compaction or surface sealing. Such conditions can lead to abnormal growth and reduced uptake or concentration of elements in a crop. Both plant and soil samples taken from the respective areas will aid in assessing corrective action. Soil samples can sometimes identify problems other than fertility as the cause of plant stress.

Apparent deficiency of N in a legume crop is often due to a deficiency of elements other than N that are essential for the N_2 fixation process. Elements that could be affecting N_2 fixation are P, K, S, Cu, Mo, Ni, or Co.

E. Evaluation of Crops on a Given Soil

Many times, farmers and their advisors will develop fertility programs and want to determine if there may be a need for further adjustments. Even though yields may be well above average, plant analysis may indicate the next limiting elements or an imbalance. A Diagnosis and Recommendation Integrated System (DRIS) analysis (mentioned below) of the plant analysis data could indicate a need to make shifts in the fertilizer program. An Illinois farmer, Herman Warsaw, has achieved corn grain yields on a test area of 23.2 Mg/ha. Periodically, he took plant samples to determine if elements were within the sufficiency range. For a 3-yr yield of more than 19.5 Mg/ha (312 bu/acre) from Warsaw's farm, R.B. Lockman (1986, personal communication) of Agrico Chemical Company Testing Laboratory in Ohio and cooperators provided ear leaf analyses data sampled at tassel which had average elemental values as follows: N, 33.7 g/kg; P, 3.77 g/kg; K 27 g/kg; Ca, 5.1 g/kg; Mg, 1.4 g/kg; S, 2.7 g/kg; B, 7.7 mg/kg; Cu, 5.7 mg/kg; Fe, 106 mg/kg; Mn, 48 mg/kg; and Zn, 27 mg/kg. Analyses were also determined on the mature grain. The average values based on dry matter were as follows: 15.7 g of N/kg, 3.2 g of P/kg, 3.1 g of K/kg, 0.3 g of Ca/kg, 1.2 g of Mg/kg, 1.3 g S/kg, 1.6 mg of B/kg, 3.1 mg of Cu/kg, 38 mg of Fe/kg, 8 mg of Mn/kg, and 41 mg of Zn/kg. These latter values readily convert to kg/Mg or g/Mg to estimate nutrient removals by the 19.5 Mg/ha grain yield.

F. Crop Logging

In crop logging, periodic analysis of seasonal samples of high value crops, such as sugarcane (*Saccharum officinarum* L.), sugarbeet, and pineapple [*Ananas comosus* (L.) Merr.], is used so that nutrient additions can be made if an element or elements drop below the optimum or sufficiency levels

(Clements, 1961; Su, 1969). A detailed record is kept of weather conditions, pest infestations, and other growth-influencing factors. Baver (1961) demonstrated how crop logging and soil testing could be combined with other management practices to develop improved recommendation for sugarcane. By closely monitoring the crop to pick up stress conditions under intensive management, nutrients can be applied through irrigation systems or foliarly by ground or aerial applicators. Jones and Bowen (1981) compared crop log and DRIS diagnoses (see below) for sugarcane and found that it depended upon the element being considered which approach gave the most accurate diagnosis. However, nearly identical diagnosis would have been made by either approach for P, Ca, Mg, Mn, S, and Si. As production of field crops becomes more sophisticated, it may be that crop logging based on local values will come into wider use. Some dealerships and farmers are already using crop consultants and scouting to pick up problems earlier and to improve the timeliness of corrective actions.

G. Diagnosis and Recommendation Integrated System

The DRIS, as a system in crop production initially designed by Beaufils (1961), should be applied to both plant and soil analyses. The system was developed to determine (i) the concentrations and interrelations of essential elements in plants and (ii) the soil nutrient levels and conditions and cultural practices associated with optimum plant growth and the highest attainable yields. The system was first applied to rubber trees (*Hevea brasiliensis* L.) in Vietnam. It is based on the premise that with optimum concentrations of one or more elements, the yield level achieved may be high, low, or intermediate, depending upon one or more other factors affecting crop growth. These include availability of other nutrients, soil characteristics, water availability, temperature, plant population, weeds, insects, or diseases and cultural practices. Both the individual elemental concentrations and ratios of the elements, one to another, or their multiples can be used, and these values are divided into those from high- and low-yielding subpopulations. The high- and low-yielding subpopulations are used to determine the means or norms, coefficients of variation, variance, and standard deviations. All expressions for which a significant variance ratio (SA/SB) between the high (A) and low (B) yield subpopulations are found, are retained because these are the expressions which should be useful to determine if a nutrient(s) is/are approaching optimum levels or are deficient or excess. Few researchers have combined both the soil and plant approach to DRIS. Only recently has an effort been made to apply it to soil nutrient parameters with modest success for lower-yielding populations of soybean in the southeastern USA. (Evanylo et al., 1987; Evanylo & Sumner, 1987).

M.E. Sumner, a former colleague of Beaufils from South Africa, introduced the DRIS approach in the USA in the mid-1970s. Since then, DRIS norms have been developed for many crops, including corn or maize (Beaufils, 1973; Sumner, 1977a, b, d, 1979, 1981; Escano et al., 1981; Elwali et al., 1985; Elwali & Gascho, 1988; Walworth et al., 1988); soybean (Sumner,

1977b; Hanson, 1981; Beverly et al., 1986; Evanylo & Sumner, 1987; Hallmark et al., 1988; Hallmark, 1988); wheat (*Triticum aestivum* L.) (Sumner, 1977c, 1981; Amundson & Koehler, 1987); sugarcane (Jones & Bowen, 1981; Elwali & Gascho, 1983; Elwali & Gascho, 1984); alfalfa (Kelling et al., 1985–1986; Russelle & Sheaffer, 1986; Walworth et al., 1986); coastal bermudagrass (*Cynodon dactylon* L.) (Tarpley et al., 1985; Robinson & Tarpley, 1986); potato (Beaufils, 1973; MacKay et al., 1987; Evanylo & Zehnder, 1988); tobacco (*Nicotiana tabacum* L.) (Evanylo et al., 1988a, b); sweet cherry [*Prunus avium* (L.)]; and filbert (*Corylus avellana* L.) (Righetti et al., 1988a, b). The DRIS has also been applied to fir trees [*Abies fraseri* (Pursh) Poir.] (Hockman et al., 1989) for evaluating nutrient balance for Christmas tree quality.

The DRIS approach as applied to plant analysis allows the researcher or diagnostician to place a relative ranking of the element from the most to the least deficient and calculate an index based on the sum of the positive and negative values found for the various nutrients. The DRIS analysis has been found in some cases to be more sensitive than the critical or sufficiency level in identifying the need for higher levels of one or more nutrients or nutrient balance problems. Some public and private laboratories are now using graphic printouts as well as numerical values to indicate the degree of deficiencies or excess of nutrients, such as were proposed by Tarpley et al. (1985).

Because DRIS uses ratios of nutrients, dry matter dilution due to crop maturity is minimized and time of sampling should be less important (Sumner, 1977a). Apparently, the results are somewhat dependent upon the crop. Evanylo et al. (1988a) found that they could make precise diagnoses for tobacco with tissue sampled either early or late if many nutrients are considered simultaneously. Amundson and Koehler (1987) indicated that for wheat, sampling at early heading provided the most correct diagnoses. Hallmark et al. (1988) found that physiological age was important and that more accurate diagnoses were made when plants sampled at the same growth stage were used as the database. Also, there is evidence that for properly developed norms, the portion of the plant sampled becomes less important. However, one should sample the portion most likely to reflect the nutritional status of the crop.

Initially, it was suggested that DRIS norms for different crops established at one geographic location should be applicable to other regions. Results of studies on corn, soybean, alfalfa, wheat, and potato have indicated that norms developed locally or regionally produced more accuracy in diagnosing deficiencies than those from other regions (Escano et al., 1981; Beverly et al., 1986; Walworth et al., 1986; Amundson & Koehler, 1987; MacKay et al., 1987). Within a region, the degree of accuracy has proven to be rather high in predicting likely responses to nutrients based on experimental results (Tarpley et al., 1985).

Researchers are beginning to test the validity of early sampling using both critical levels and DRIS to see if they can detect seasonal nutrient shortages and increase nutrient efficiencies by delayed applications (Elwali & Gascho, 1988). It is expected that research of this type will increase, espe-

cially with elements that may be related to environmental problems. Also, researchers are comparing norms generated from a few high-yielding experiments provided from a relatively small database, with those from a broader or worldwide database (Walworth et al., 1988). From the initial comparison, it appears that more diagnostic accuracy may be obtained from norms developed from the high-yielding database. Combinations of DRIS and modified-DRIS (M-DRIS) norms using nutrient ratios and dry matter concentrations from full-bloom trifoliolate leaf samples from soybean yielding > 3.5 Mg/ha (52 bu/acre) indicated that M-DRIS norms were especially helpful in correctly diagnosing nutrients that were not deficient (Hallmark, 1988). The DRIS norms were most useful in correctly diagnosing situations where P and K were most deficient.

Even though some claim that there is little physiological basis for some of the ratios used in DRIS (Smith, 1986), it is a system that provides the possibility of bringing all of the elements involved in nutrition together and evaluating them simultaneously, with yield level being part of the process. Hence, it should provide an improved opportunity to look at nutrient balance. While DRIS is not perfect, it often provides a better estimate for predicting nutrient shortages and responses than the critical level or sufficiency concepts. The latter estimates identify the most-limiting nutrient or nutrients, which must be supplied before the sufficiency of other elements can properly be evaluated. The DRIS is designed to overcome this limitation, using the ratio norms to place an order on the second, third, or fourth most limiting nutrients.

Karlen et al. (1988) applied DRIS norms to corn results in which Flannery had produced 19.3 Mg/ha (308 bu/acre) of grain and found that all but four of the indices were within $+/- 18$ for most of the samplings. These indices apparently indicate relatively good nutrient balance. It is probable that the use of DRIS will continue to increase. If adequate calibration data are available and properly evaluated, the sufficiency level and DRIS approaches should in the long-run provide similar answers to diagnosticians' questions.

Some experiment stations now have copyright computer diskettes available for DRIS analysis of various crops, enhancing the availability and use of the programs. The University of Georgia is one such institution. Many soil and plant analysis laboratories now provide a DRIS analysis when returning the plant analysis results to the customer.

H. Determination of Total Nutrient Uptake of High-Yielding Crops

One of the major functions of plant analysis is to determine the uptake and use of various nutrients by different crops over the season and at maturity. Knowing the amounts of nutrients taken up at various times during the season is important because uptake is rate driven, with peak periods of nutrients required, depending upon the developmental stages of growth. These peak demands for high yields may not be met by many soils unless greater-than-normal levels of nutrients are present or special applications of some

are provided. The total uptake during different periods helps determine the quantities that must be provided by the soil and fertility program, and the amounts that will be removed by the harvested crop. The latter values, long-term, help determine the maintenance amounts of nutrients to maintain or increase yields and fertility of soils.

Rhoads and Stanley (1981, 1984); Flannery (1986a, b); and Karlen et al. (1985, 1987, 1988) have determined the nutrient uptake of high-yielding corn. Karlen et al. (1988) found that for a corn crop yielding 19.3 Mg/ha (308 bu/acre), the greatest amounts of nutrients per hectare in the aerial portion of the crop were: N, 386 kg; P, 70 kg; K, 370 kg; Ca, 59 kg; Mg, 44 kg; S, 40 kg; B, 0.13 kg; Cu, 0.14 kg; Fe, 1.9 kg; Mn, 0.8 kg; and Zn, 0.8 kg. Flannery (1986a) found that average rates of nutrient uptake for N, P, and K during a 13-d period between the 12th leaf and early tassel stages of growth were 12.38 kg ha⁻¹ d⁻¹ of N, 1.39 kg ha⁻¹ d⁻¹ of P, and 14.24 kg ha⁻¹ d⁻¹ of K. During that 13-d period, the crop accumulated about 42% of its N, 26% of its P and >50% of its K. Karlen et al. (1987) found that peak accumulation rates for N, P, and K were 10, 1.6, and 28 kg ha⁻¹ d⁻¹, respectively, at a growth stage associated with 550 growing degree units for corn that yielded 14 Mg/ha.

Henderson and Kamprath (1970), Hanway and Weber (1971), Terman (1977), Karlen et al. (1982), and Flannery (1986b) have studied dry matter and nutrient accumulation during the growth and development of soybean. The bean yields ranged from 4.77 (Terman) to 5.38 (Henderson and Kamprath) to 6.79 (Flannery) Mg/ha in the respective studies. In Flannery's study, the highest total aerial uptake of nutrients were as follows: N, 614 kg; P, 64.6 kg; K, 402 kg; Ca, 185 kg; Mg, 63 kg; and S, 31 kg. The peak rate of uptake of N was 12.8 kg ha⁻¹ d⁻¹ during a 21-d period between pod development and soft seed. Forty-four percent of the total N was taken up during that period. For P, the highest rate of uptake occurred during the same period as the N, and was 1.35 kg ha⁻¹ d⁻¹, with the same percentage of the total taken up as for N. The highest rate of K uptake occurred between full bloom and pod development, from the 67th to 82nd day following emergence, and was 8.92 kg of K ha⁻¹ d⁻¹. Between the 51st and 82nd day, more than 213 kg of K or nearly 55% of crops total K was taken up.

Total nutrient uptake values have been determined for wheat yielding more than 11 Mg/ha (Brown, 1986), lowland rice grain (*Oryza sativa* L.) yielding 9.8 Mg/ha (DeDatta & Mikkelsen, 1985), alfalfa yielding from 17.9 to more than 20 Mg/ha (Tesar, 1981; Lanyon et al., 1983), potato crops yielding 79 Mg/ha (Roberts & McDole, 1985), cassava (*Manihot esculenta* Crantz) with a fresh root yield of 52.1 Mg/ha (Howeler, 1985), and cauliflower (*Brassica oleracea* L.) yielding 17.9 Mg/ha of curd (Welch et al., 1987). Practitioners desiring these data should check those papers for details.

For high-yielding crops, the uptake per megagram of crop produced or the nutrient removal per megagram of crop harvested will often be nearly constant. There is less variation in the elemental content of the harvested grain than in portions that may be left in the field. For example, Bundy and Oplinger (1984) found that when yields of soybean were increased from 4.4

Table 14-2. Concentrations of nutrients in soybean seed at two yield levels and row widths (Bundy & Oplinger, 1984).

Soybean Row yield width	Nutrient concentration in seed									
	N	P	K	Ca	Mg	S	Zn	B	Mn	Cu
Mg/ha cm	g/kg					mg/kg				
5.846 20.3	58.5	6	17.9	1.9	2.4	3.1	41	26	25	10
4.435 76.2	58.3	6	18.0	2.0	2.3	3.0	43	27	25	11

to more than 5.8 Mg/ha by narrowing the row spacing, the elemental concentrations of the different nutrients in the seed for the two yield levels remained nearly constant (Table 14-2), but the removal of nutrients was, of course, greater for the higher yield level.

Gill and Kamprath (E.J. Kamprath, 1987, personal communication) conducted research on rice in Sumatra and found that with increasing rates of applied K, the K concentration of the grain only ranged from 2.9 to 3.1 g/kg, the higher value being on the control plots, while the grain dry matter yield was increased 1.65 Mg/ha. A high correlation was found between the rice yield and the K concentration in the straw at harvest ($r = 0.90$).

For forages, such as alfalfa, it is relatively easy to evaluate the nutrient requirements per unit of production or efficiencies of nutrients. In a study in which rates of K and irrigation levels were used to increase yields, at the two highest levels of production, Sheaffer (1984) found the results shown in Table 14-3. Even though there was more than a 4.7 Mg/ha differential in dry matter yield, the nutrient concentrations for the two yield levels did not differ significantly. By taking the reciprocal of the values presented, the internal efficiencies for the different nutrients are determined.

III. THE FUTURE

While plant analysis has not proven to be the panacea that some had hoped in pointing the way to higher yields or solving soil fertility problems, it is nevertheless an important tool in our diagnostic arsenal. In many cases where the answers to soil fertility problems are fairly simple, it is extremely effective. However, in cases where problems are more complex, application of DRIS, which allows one to evaluate the relationships among nutrients, may provide a better approach. If DRIS can provide better answers than the critical level or sufficiency range, it will probably become the system or

Table 14-3. Alfalfa nutrient uptake per Mg of dry matter (DM) produced at two yield levels (Sheaffer, 1984).

Alfalfa yield-DM	Nutrient uptake of dry matter								
	N	P	K	Ca	Mg	Zn	B	Cu	Mn
Mg/ha	kg/Mg								
13.7	29	2.2	29.0	15.5	2.55	0.02	0.05	0.01	0.055
9.96	31	2.15	24.5	16.0	2.75	0.02	0.055	0.01	0.070

approach of choice. The DRIS norms, once developed, can easily be entered into computers so that the analysis is readily available to both laboratories and individuals.

Extension specialists and agents, as well as, dealers and consultants are becoming more computer literate and sophisticated in their operations. They are now using plant analysis more at all production levels. They can have information available at the flick-of-a-switch and can access communication networks that were only dreamed of a few short years ago. While some farm-supply consulting groups have chosen to back off from their initial goal of putting many crop consultants in the field, indications are that the number of private consultants will continue to increase. This will be in response to farmer demand for special attention in their specific production systems, seasonal monitoring, and improvement of nutrient use efficiency for rational optimum yields. More attention will be given to matching genotypes, soil fertility, and cultural management programs. This approach will help balance economic and environmental considerations.

The challenge for researchers and producers is to determine how to produce a bigger package or yield in a given time frame, for a single crop or with multiple cropping. As has been shown through the application of plant analysis in high-yield research, such systems place special nutrient stress on soils in terms of rates, processes, and nutrient availabilities during peak periods of uptake. In the future, large gains will be made in crop production. Study of quantum mechanics and randomness of our system indicate that striking accomplishments are likely in many fields, including agriculture, especially as new genotypes become available from biotechnology. The soil fertility and plant nutrition researchers must be part of that technology to analyze and test the new lines that result from that effort. Plant analysis will play a key role in future studies.

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Chapter 15

Sampling, Handling, and Analyzing Plant Tissue Samples

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Plant analysis (sometimes referred to as leaf analysis) is the determination of the total elemental content of a specified plant part. The emphasis in this chapter will be on the determination of those elements required for plant growth. Interpretation is normally based on the use of a “critical value” or “sufficiency range” (Smith, 1962) comparison between the elemental concentration found and a known norm (Goodall & Gregory, 1947; Chapman, 1966; Reuter & Robinson, 1986; Adriano, 1986; Martin-Prevel et al., 1987). An alternative method of interpretation is Diagnosis and Recommendation Integrated System (DRIS), which interprets the ratios of elements (N/P, K/Ca, and K/Mg) as indicators of elemental status (Beaufils, 1973; Sumner, 1977, 1982).

Most growers primarily use a plant analysis for diagnosing suspected elemental insufficiencies, while its most significant, yet little used application, is for evaluating the soil/plant elemental status. This is partially reflected in the relatively few plant tissue samples assayed for growers, about 500 000, in the USA each year (Jones, 1985). Tissue testing, an elemental assay of extracted cell sap by means of quick chemical tests in the field, seems to be gaining an interest at levels equal to that observed several decades ago.

A plant analysis is carried out in a series of steps as shown in Fig. 15-1. The results obtained are no better than the care taken in collecting, handling, preparing, and analyzing the collected tissue. An error made in one of these steps can result in an erroneous interpretation leading to recommendations that may be either unnecessary, costly, or even damaging to the crop. Therefore, it is important for those employing either a plant analysis or tissue test to follow the proper sampling, preparation, and analysis procedures. This chapter deals with the procedures required to successfully conduct a plant analysis or tissue test.

PLANT ANALYSIS

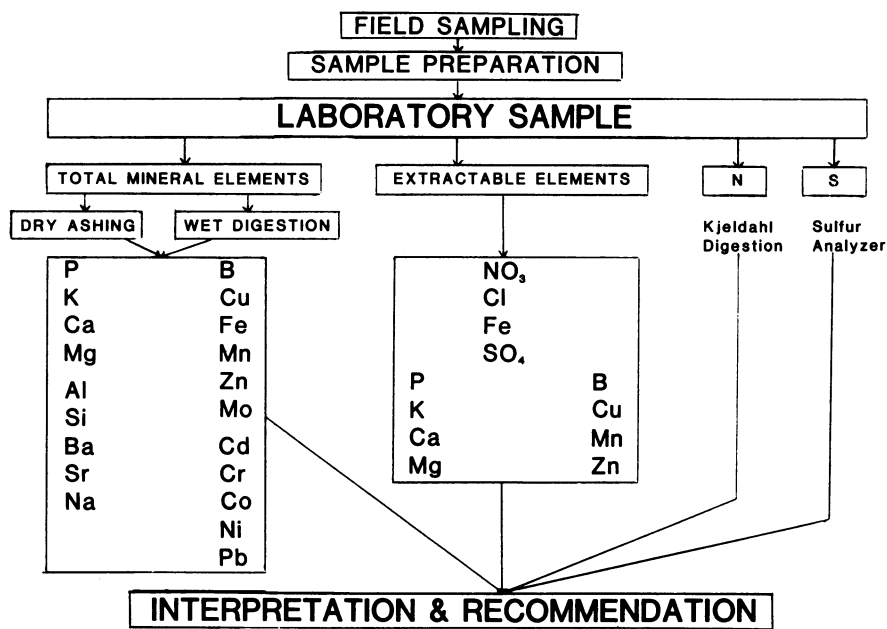


Fig. 15-1. Sequence of procedures for conducting a plant analysis.

I. SAMPLING

The validity and usefulness of the determined elemental content of a collected plant tissue sample hinge upon an intelligent and realistic approach to the problem of how to obtain a reliable sample. If the sample taken is not representative of the general population, all the careful and costly work put into the subsequent analysis will be wasted because the results will be invalid. To obtain a representative sample from a particular plant species is a complex problem, and expert knowledge is required before it can be attempted.

A. Elemental Heterogeneity

The elemental content of a plant is not a fixed entity, but varies from month to month, day to day, and even from hour to hour on the same day as well as differing among the various parts of the plant itself (Goodall & Gregory, 1947; Jones, 1970). A specific plant part at a definite location on the plant obtained at a definite stage of growth (on the basis of physiological age) constitute the sampling parameters. In general, tissues that are either physiologically young and undergoing rapid change in elemental content, or those past full maturity should not be sampled.

The plant part selected and the time of sampling must correspond to the best relationship that exists between its elemental content and yield, or the physical appearance of the plant (Bates, 1971). Frequently, no single time for sampling of a particular plant part is ideal for evaluating every element. Therefore, several plant parts at different growth stages may need to be taken. Comparisons of analyses between leaves and petioles, stems and leaves, and upper and lower plant parts may assist in evaluating a plant analysis (Bates, 1971). Jones (1967) noted that the determination of the homogeneity, or the lack of it, may be a useful technique when diagnosing certain suspected elemental deficiencies in some crops. For example, corn (*Zea mays* L.) plants deficient in K contain less K in their lower leaves than in their upper leaves. When plants contain sufficient K, the reverse is true. It was also noted that differences in concentration of B and Zn among the upper and lower leaves of corn decrease as the plant approaches B or Zn deficiency (Jones, 1967). However, the practical application of this technique of comparison of analysis results between plant parts has yet to develop into a practical system of plant analysis interpretation.

B. Statistical Considerations

Once it has been determined what plant part is to be sampled to represent the plant's elemental status, the number of plants to sample for adequate representation must be decided. What constitutes an adequate number has been determined to some degree from the results of previous research.

Plants growing adjacent to each other can differ considerably in their elemental content. Lilleland and Brown (1943), when studying the P nutrition of peach (*Prunus persica* L.) trees, found that the composition of morphologically homologous leaves taken from adjacent trees receiving the same fertilizer treatment differed considerably. This was also the experience that Thomas (1945) found with apple (*Malus sylvestris* Mill.) trees, and Steyn (1959) with citrus trees and pineapple [*Ananas comosus* (L.) Merr.] plants.

Elemental content variations within single plant parts as well as from plant to plant must be considered. Steyn (1959) has shown that there are relatively small variations in the N, P, K, Ca, Mg, Fe, Mn, Zn, and Cu concentration among the selected sampling material on a single citrus tree or a single pineapple plant. It is reasonable to assume that this could be the case for other plants as well. Therefore, provided the sampled material is carefully selected, a relatively small sample could adequately represent the elemental content of a single plant.

When considering the variation in element content from plant to plant, the situation can be entirely different. If large variations exist, then intensive sampling is required to obtain sufficient plant tissue for representing the element content of the plant sampled. Steyn (1961) conducted a statistical sampling study on citrus trees and pineapple plants in which adjacent plants in blocks were intensively sampled under rigorously controlled conditions. Some of the analysis results from citrus trees are shown in Table 15-1. Similar trends were also observed for pineapple plants.

Table 15-1. Minimum number of trees (in blocks of 16 trees) to sample to show a 5% level significance in differences (D) exceeding D% of the mean values (Steyn, 1961).

Item	Element								
	N	P	K	Ca	Mg	Fe	Mn	Zn	Cu
	g kg^{-1}						mg kg^{-1}		
Mean	26.8	1.17	4.8	36.3	4.8	80.0	23.4	11.0	5.9
CV, %	5.3	3.6	15.8	7.2	18.3	8.0	16.9	20.0	18.3
	Number of trees								
D=10%	3	2	23	5	31	6	26	37	31
D=20%	1	1	6	2	8	2	7	10	8

It was found that, when the citrus trees were in poor condition, much more intensive sampling than that shown in Table 15-1 was necessary for adequate representation. In this study, variation in N and P content was usually considerably less than that observed for the other elements. Potassium and Mg showed the greatest degree of variation, followed by some of the micronutrients, such as Cu and Zn. When the concentration of the element was at a deficient level, the variation was exceptionally large. This is evident for Zn as shown in Table 15-1 where virtually all the trees in the block of 16 would have to be sampled for adequate representation of plant Zn status. Similar results were obtained in the pineapple sampling study. Therefore, if all the essential elements are to be determined in a single sample, a requirement to adequately interpret a plant analysis is to follow an intensive sampling procedure. As was observed for citrus, many leaf tissue samples would be required if pineapple plants under nutrient element stress were being evaluated for their elemental content.

Colonna (1970), working in a homogeneous coffee (*Coffea arabica* L.) plantation, recommended sampling two leaves per tree from 40 randomly selected trees per hectare in 1 ha. In fertilizer trials, he found it necessary to sample five to six replicates with 20 to 25 coffee plants per treatment to obtain useful plant analysis data. Similar sampling studies for the more commonly grown annual field crops have yet to be done to establish the sampling intensity required to ensure reasonable analytical reliability.

C. Tissue Sampling Techniques

Kenworthy (1969), Chapman (1964), and Jones et al. (1971) have summarized sampling techniques that have been generally accepted for interpreting plant analyses. A list of recommended sampling procedures is given in Table 15-2. If other sampling procedures are used, interpretation of the plant analyses data may differ. Since there is a substantially large potential for errors to occur due to improper sampling technique, only thoroughly trained and experienced technicians should be responsible for collecting tissue samples in the field. The number of plants to sample in a particular situation depends on the general condition of the plants, soil homogeneity, and the purpose for which the analysis result will be used. To ensure representa-

Table 15-2. Suggested sampling procedures for field and vegetable crops, fruit and nuts, and ornamentals (Jones et al., 1971).

Crop	Stage of growth	Plant part to sample	Number of plants to sample
<u>Field crops</u>			
Corn	Seedling stage (< 12 in.)	All the aboveground portion	20-30
	Prior to tasselling	The entire leaf fully developed below the whorl	15-25
	From tasselling and shooting to silking	The entire leaf at the ear node (or immediately above or below it)	15-25
Soybean or other bean	Seedling stage (< 12 in.)	All the aboveground portion	20-30
	Prior to or during flowering*	Two or three fully developed leaves at the top of the plant	20-30
*Sampling after pods begin to set not recommended			
Small grain (including rice)	Seedling stage (< 12 in.)	All the aboveground portion	50-100
	Prior to heading	The fourth uppermost leaves Sampling after heading is not recommended	50-100
Hay, pasture or forage grasses	Prior to seed head emergence or at the optimum stage for best quality forage	The fourth uppermost leaf blades	40-50
Alfalfa	Prior to or at 1/10 bloom stage	Mature leaf blades taken about one-third of the way down the plant	40-50
Clover and other legumes	Prior to bloom	Mature leaf blades taken about one-third of the way down the plant	40-50
Sugarbeets	Mid-season	Fully expanded and mature leaves midway between the younger center leaves and the oldest leaf whorl on the outside	40-50
Tobacco	Before bloom	Uppermost fully developed leaf	8-12
Sorghum-milo	Prior to or at heading	Second leaf from top of plant	15-25
Peanuts	Prior to or at bloom stage	Mature leaves from both the main stem and either cotyledon lateral branch	40-50
Cotton	Prior to or at first bloom or when first squares appear	Youngest fully mature leaves on main stem	30-40
<u>Vegetable crops</u>			
Potato	Prior to or during early bloom	Third to sixth leaf from growing tip	20-30
Head crops (cabbage, etc.)	Prior to heading	First mature leaves from center of whorl	10-20
Tomato (field)	Prior to or during early fruit set	Third or fourth leaf from growing tip	20-25

(continued on next page)

Table 15-2. Continued.

Crop	Stage of growth	Plant part to sample	Number of plants to sample
<u>Vegetable crops</u>			
Tomato (Greenhouse)	Prior to or during fruit set	Young plants: Leaves adjacent to second and third clusters	20-25
		Older plants: Leaves from fourth to sixth clusters	20-25
Bean	Seedling stage (< 12 in.)	All the aboveground portion	20-30
	Prior to or during initial flowering	Two or three fully developed leaves at the top of the plant	
Root crops (carrots, onions, & beets, etc.)	Prior to root or bulb enlargement	Center mature leaves	20-30
Celery	Mid-growth (12-15 in. tall)	Petiole of youngest mature leaf	15-30
Leaf crops (lettuce, spinach, etc.)	Mid-growth flowering	Youngest mature leaf from the top of the plant	35-60
Peas	Prior to or during initial flowering	Leaves from the third node down	30-60
Sweet corn	Prior to tasselling	The entire fully mature leaf below the whorl	
	At tasselling	The entire leaf at the ear node	20-30
Melons (water, cucumber, & muskmelon)	Early stages of growth prior to fruit set	Mature leaves near the base portion of plant on main stem	20-30
<u>Fruits and nuts</u>			
Apple, apricot, almond, prune, peach, pear, cherry	Mid-season	Leaves near base of current year's growth or from spurs	50-100
Strawberry	Mid-season	Youngest fully expanded mature leaves	50-75
Pecan	6 to 8 wk after bloom	Middle pair of leaflets from mid-portion of terminal growth	30-45
Walnut	6 to 8 wk after bloom	Middle pair of leaflets from mature shoots	30-35
Lemon, lime	Mid-season	Mature leaves from last flush or growth on nonfruiting terminals	20-30
Orange	Mid-season	Spring cycle leaves, 4 to 7 mo old from nonbearing terminals	20-30
Grapes	End of bloom period	Petioles from leaves adjacent to fruit clusters	60-100

(continued on next page)

Table 15-2. Continued.

Crop	Stage of growth	Plant part to sample	Number of plants to sample
Fruits and nuts			
Raspberry	Mid-season	Youngest mature leaves on lateral or "primo" canes	20-40
Ornamentals and flowers			
Ornamental trees, shrubs	Current year's growth	Fully developed leaves	30-100
Turf	During normal growing	Leaf blades; clip by hand to avoid contamination with soil or other material	¼ liter of material
Roses	During flowering production	Upper leaves on the flowering stem	20-30
Chysanthemums	Prior to or at flowering	Upper leaves on flowering stem	20-30
Carnations	Unpinched plants	Fourth or fifth leaf pairs from base of plant	20-30
	Pinched plants	Fifth and sixth leaf pairs from top of primary laterals	20-30
Poinsettias	Prior to or at flowering	Most recently mature fully expanded leaves	15-20

tion, sampling as many plants as practical is recommended, collecting samples during a particular time of day and under calm climatic conditions.

As a general rule, mature leaves exposed to full sunlight just below the growing tip on main branches or stems are usually preferred, taken just prior to or at the time the plants begin their reproductive stage of growth. In some situations, sampling may be necessary at earlier periods in the plant's growth cycle with the same maturity.

There are as many instructions on what *not* to sample as there are on what to sample. For example, do not collect tissue that is covered with soil or dust, or from plants damaged by insects, mechanically injured, or diseased. Dead plants should not be sampled, or dead tissue included as a part of a collected sample. Whole plants or plants beyond full maturity should not constitute the sample or a portion of the sample. In addition, sampling is not recommended when plants are under moisture or temperature stress. Seeds are not normally useful for assessing the nutrient element status of plants, except possibly for the element N. In some instances, seed analyses have been of value in determining the Mo and Zn supply for young plants developing from that seed (Reisenauer, 1956; Shaw et al., 1954).

Plants under stress due to a possible elemental deficiency or imbalance should be sampled only at the initiation of the stress. After a period of stress, plants develop unusual element concentrations in their tissues that can lead to a misinterpretation of a plant analysis result. When visual symptoms occur,

or a deficiency is suspected, the analysis of the same plant part from adjoining normal plants in the same field or area can aid in the interpretation (Munson & Nelson, 1973). However, if the plants being compared differ in their vigor and stage of development, the same plant part at the same stage of development may not exist. Therefore, comparing the analysis results between two sets of tissues may be confusing. It is also advisable to collect soil samples from the same area where plants have been selected for sampling. Comparing analysis results between and among soil tests and plant analysis results can assist in the interpretation.

Normally, after pollination and as plants begin setting and developing fruit or seed, the elemental content of the vegetative portions of the plant begin to change substantially, making a plant analysis interpretation difficult if leaf tissue is collected at this time. Therefore, sampling after pollination is not recommended for most grain and fruit crops.

Standardizing sampling techniques cannot be over emphasized, since criteria for elemental analysis interpretation have been established for specific plant conditions. Therefore, for elemental concentration determinations to be meaningful, it is essential to adhere to the given sampling procedures designed for the plant species and element(s) to be assayed.

II. TISSUE PREPARATION

After collection, the plant tissue must be: (i) cleaned to remove surface contamination; (ii) oven dried to stop enzymatic reactions and remove moisture; (iii) reduced in particle size to homogenate and obtain a suitable laboratory sample; and (iv) finally dried to a constant weight. Two additional steps may be needed: (i) storage and transport of the fresh material prior to cleaning (decontamination) and oven drying; and (ii) storage of the dried and powdered tissue prior to analysis.

A. Decontamination

Exposed plants are always covered with a thin film of dust that is difficult to remove by mechanical wiping or brushing. Failure to remove this dust normally affects only the determinations for Fe and Al unless the dust cover is considerable or of a specific composition. Leaf material may be contaminated with spray residues, whether applied for nutritional, insecticidal, or fungicidal purposes (Ashby, 1969). Therefore, these sources of contamination that will affect the analytical result must be removed when the leaf material is fresh. Steyn (1959) and Wallace et al. (1980) found that the only satisfactory way of removing contamination is by washing the tissues in a 0.1 to 0.3% detergent solution followed by rinsing in pure water. Sonneveld and van Dijk (1982) recommend dipping tissue for 15 s into an ample volume of solution containing 1% Teepol (detergent) and 0.1 *M* HCl, followed by rinsing in pure water. The washing procedure must be done quickly to avoid long contact between the solution and tissue as there is the danger that some

elements, such as K and Cl, will be removed by leaching (Bhan et al., 1959). Smooth leaves can be easily wiped with a damp cloth or washed to decontaminate, while, leaves that are pubescent or not smooth surfaced are difficult, if not impossible, to decontaminate completely. The effect that washing can have on the elemental content of orange [*Citrus sinensis* (L.) Osbeck], corn, and apple leaves are shown in Table 15-3.

Unless leaf tissue is visually coated with dust or other foreign substances, washing to remove these substances is usually not necessary. The only exception would be when Fe (Wallace et al., 1982) as well as Al and Si are determined elements. If the plant material is not washed, the method of organic matter destruction (procedures that are discussed in more detail later) may also affect the analysis for these three elements.

B. Oven Drying

After washing (decontamination), the plant tissue must be dried as rapidly as possible to minimize chemical and biological change. If drying is unduly delayed, considerable loss in dry weight may occur due to respiration (Lockman, 1970), while proteins will be broken down to simpler nitrogenous compounds with the potential release of ammonia. Also, a too high drying temperature can affect the dry weight (Grant & MacLaughlin, 1968). Dry weight preservation is essential since element content is expressed on a dry weight basis of prepared tissue.

The requirements that must be satisfied when drying plant material are that the temperature is sufficiently high to destroy the enzymes responsible for decomposition and sufficient for moisture removal yet below the temperature of thermal decomposition. According to Tauber (1949), enzymes present in plant tissue are rendered inactive at temperatures above 60°C. Therefore, air drying plant tissue prior to more than 1 or 2 d of storage, particularly if the tissue was previously washed, may not be sufficient to prevent enzymatic decomposition from occurring. Therefore, tissue should be dried quickly in a dust-free, forced-draft electrical oven as soon after collection as possible. Steyn (1959) determined the extent of losses over 8 wk when citrus and pineapple leaves were dried in a forced-draft oven set at 50, 65, and 105°C, respectively. The samples were dried for 24 h and weighed. The results are shown in Table 15-4. Drying at 50°C was not sufficient as there was enough retained moisture for enzymatic action to occur during storage. Drying at 65°C resulted in a certain amount of thermal decomposition, but enzymatic action was successfully stopped even after 8 wk storage.

During the particle-size reduction process, previously oven-dried plant tissue will absorb varying amounts of moisture that must be removed before weighing the tissue for analysis. Because of the difference in physical state between plant tissue powder and the unground material, a similar drying experiment as that described above was carried out by Steyn (1959) on plant tissue powder.

Steyn (1959) found much greater thermal decomposition when leaf powder was dried at the higher temperatures than when the plant tissue was

Table 15-3. Element concentration in orange, corn, and apple leaves as affected by washing.

Element	Orange leaves†			Corn leaves				Apple leaves¶	
	Unwashed	Detergent washed	Detergent plus acid washed	Unwashed‡	Wiped with detergent solution†	Unwashed§	Washed in distilled water§	Unwashed	Washed with detergent
	g kg ⁻¹								
Ca	39.7	39.7	39.6	8.7	8.5	4.8	4.5	--	--
K	10.7	10.8	20.4	21.7	21.7	12.2	12.6	17.8	18.0
Mg	4.2	4.1	4.2	1.6	1.6	3.9	4.1	2.5	2.3
N	25.3	25.6	25.5	--	--	29.3	31.1	22.2	21.9
P	1.5	1.5	2.7	--	--	2.2	2.2	--	--
	mg kg ⁻¹								
B	367.0	368.0	369.0	17.0	17.0	11.0	10.0	28.0	27.0
Cu	5.6	5.1	5.0	29.5	28.8	9.0	10.0	--	--
Fe	186.0	61.0	61.0	136.0	134.0	96.0	85.0	77.0	72.0
Mn	182.0	94.0	92.0	--	--	73.0	64.0	38.0	36.0
Mo	--	--	--	--	--	1.1	1.2	--	--
Zn	123.0	68.0	65.0	23.1	30.5	22.0	22.0	14.1	15.6

† Labanauskas (1968).

‡ Baker et al (1964).

§ Jones (1963).

¶ Ashby (1969).

Table 15-4. Loss of weight of fresh leaves at constant temperature (Steyn, 1959).†

Time, h	Loss in wt., %					
	Citrus leaves			Pineapple leaves		
	50°C	65°C	105°C	50°C	65°C	105°C
5	41.9‡	57.7‡	58.5§	24.0§	34.1§	90.5¶
10	56.7	57.9	58.5	58.5	90.1	90.7
24	57.2	58.0	58.7	86.4	90.2	90.7
48	57.5	58.2	58.9	88.7	90.3	90.9
72	57.6	58.2	59.0	89.0	90.4¶	91.3
96	57.7	58.2	59.1	89.1	90.6	91.6
168	57.8‡	58.2§	58.5¶	89.5§	90.9¶	92.0¶
14 d	57.8	58.2	59.5	89.7	90.9	92.1
30 d	58.3	58.2	59.5	91.0	90.9	92.1
60 d	58.8	58.3	59.5	92.0	90.8	92.1

† Difference > 0.4% is significant.

§ Slight scorching, dull-brown mottling.

‡ No scorching, fresh leaf color.

¶ Severe scorching, brown throughout.

dried in its original physical state at the same temperatures, indicating the sensitivity of the finely divided state of the powder to drying temperature compared to the original material (Table 15-5). Consequently, the prevailing tendency of workers to dry ground plant tissue at 105°C prior to analysis must be questioned. As shown in Table 15-5, a 2% difference in the dry weight of citrus leaf powder was obtained between the 65 and 105°C drying temperature in a 24-h period. For the pineapple leaf powder, the difference in dry weight amounted to more than 5.5% in the same 24-h period. Whereas a certain degree of variation in oven temperature when drying fresh plant material may be permissible, oven temperature must be strictly controlled for tissue powder which is more susceptible to thermal decomposition.

Steyn's results would suggest that oven drying plant tissue powder at 65°C for 24 h removes moisture without thermal decomposition. However, Bowen (1967) recommended drying a hygroscopic kale powder sample at 90°C for 20 h to obtain the dry weight. Evidently, the ideal drying temperature for powdered samples is dependent on the source of the plant material and exists between 65 to 90°C. Drying fresh and powdered plant tissue at 80°C

Table 15-5. Loss of weight of leaf powder at constant temperature (Steyn, 1959).

Time, h	Loss in wt., %†			
	Citrus leaf powder		Pineapple leaf powder	
	65°C	105°C	65°C	105°C
2	4.09	5.79‡	--	--
4	4.25	5.92	2.33	4.81‡
8	4.35	5.94	2.40	6.03
16	4.40	6.30	2.40	7.00
24	4.42	6.36	2.42	7.99
48	4.47	6.48	3.01‡	9.35§
96	4.64	6.68	--	--
168	4.64	7.16§	3.08	12.30

† Difference > 0.2% is significant.

‡ Severely, scorched.

§ Blackish brown.

may be the best compromise temperature, although testing may be necessary to determine the appropriate drying temperature to minimize thermal decomposition.

For plant tissue high in soluble sugars, moisture removal is best done by either freeze drying or vacuum drying (Horwitz, 1980).

Plant tissue may be quickly and satisfactorily dried in a microwave oven (Carlier & van Hee, 1971; Shuman & Rauzi, 1981), although the procedure is somewhat tedious and not suited for drying large quantities of material at one time.

C. Particle-Size Reduction

Particle-size reduction of the dried plant material before analysis provides both a suitable form of the sample for manipulation in the laboratory as well as one of uniform composition. Because of the laborious nature of either hand cutting or crushing of dried tissue, particularly when the sample size is large, mechanical devices are normally used. These mechanical devices use either a cutting action, such as with the Wiley or hammer-type mills, or a crushing action obtained when using ball mills, or by abrasion in cyclone or UDY mills. In most mills, particles of the contact surfaces such as Cu and Zn from brass fittings, Fe from steel, Al from Al-made parts, Na and Zn from plastic seals, and Zn from rubber seals will be added to the tissue sample during the milling process. The extent of these elemental additions will depend on the condition of the mill and the length of contact time. When plant tissue samples are to be assayed for their Fe content, either hand cutting or crushing in an agate mortar are probably the only suitable techniques for reducing the particle size. No matter what device is used, test samples should be assayed to determine what elemental additions will occur during the particle-size reduction procedure.

Hood et al. (1944) determined the extent of elemental contamination occurring during the milling of plant samples. The types of milling equipment tested were a (i) Wiley mill, (ii) hammer mill, (iii) jar mill with flint, and (iv) porcelain mill with mullite balls. They found that with all four commonly used mechanical mills some degree of contamination with one or more elements (Al, Cu, Fe, and Zn) occurred. A similar study by Grier (1966) found Wiley-type mills in wide use. He recommended the use of stainless steel as the best substance for the cutting and sieving surfaces to minimize elemental contamination.

Steyn (1959) conducted a similar investigation using a Vetter agate ball mill. A composite citrus leaf sample was washed, dried, and divided into two sets of triplicate subsamples. One subsample was crushed in an agate mortar and the other was ground for 2 h in an agate ball mill. Each subsample was assayed separately. Because no significant contamination was evident in the analysis results (Table 15-6), Steyn concluded that grinding plant tissue in agate is preferred to other methods, particularly when the micronutrients are to be included in the assay.

Table 15-6. Nutrient concentration of citrus leaves after crushing and mechanical grinding in agate (Steyn, 1959).

Element	Method of grinding	
	Crushing	Mechanical grinding
	<hr/> g kg ⁻¹ <hr/>	
N	24.6	24.3
P	1.21	1.22
K	5.6	5.6
Ca	36.7	36.6
Mg	5.8	5.7
	<hr/> mg kg ⁻¹ <hr/>	
Fe	65.0	64.0
Mn	32.0	33.0
Zn	15.0	15.0
Cu	3.4	3.3

The significance of fineness of grinding using a Wiley mill has been investigated. Nelson and Boodley (1965) obtained separation of terminal and basal leaf particles during grinding and weighing. They recommended fine grinding (<20 mesh) and control of electrostatic charge which frequently arises during grinding. Smith et al. (1968) noted variation in the element concentration for various sample size fractions. For example, Zn tended to be concentrated in the larger sized fractions of barley (*Hordeum vulgare* L.) straw and alfalfa (*Medicago sativa* L.) tissue. Jones (1963) found that fractions of ground, unwashed corn leaves screened to pass 20-, 40-, 60-, and 100-mesh sieves varied in composition for the elements Fe and Zn. For example, the tissue passing the 100-mesh sieve contained four times as much Fe as the whole sample. But, this could have been due to contamination since the finer fraction probably contains more dust particles than the coarser fractions.

Fineness can be of considerable importance since it relates to sample homogeneity. Particle-size reduction to pass a 20-mesh screen is sufficient if 0.5 g or larger aliquots of plant tissue are to assayed. If < 0.5 g aliquots are taken, then particle-size reduction to pass a 40-mesh screen is necessary. Particle-size reduction that results in a wide range of particle sizes poses problems in homogeneity if the prepared tissue sample segregates during handling and weighing.

Adherence of fine particles to the cutting surface in a Wiley-type cutting mill can be partially overcome by attaching a vacuum system to the mill (Graham, 1972) or by using pulsing air (Ulrich, 1984) as well as by controlling static electricity (Nelson & Boodley, 1965).

Similar studies on particle-size distribution have not been done using ball mills or cyclone (UDY) mills for particle-size reduction. However, plant tissue processed through these types of mills are usually finer and more uniform in particle size than that obtained by cutting in Wiley-type mills.

Another complication is that some types of plant tissues are not easy to grind in a Wiley-type mill due to either the presence of pubescence (such

Table 15-7. Decomposition of fresh citrus leaves on storage (Steyn, 1959).

Storage, d	Loss in dry wt., %		
	In sealed polyethylene	Open to atmosphere	In freezer at -5°C
2	1.8	1.4	0.0
4	2.7	1.7	0.0
7	5.5	2.0	0.3
14	9.7	2.8	0.4

as on apple leaves), or when the tissue is coarse and fibrous (continuing the grinding process until the entire sample passes through the mill) or the tissue is highly deliquescent. Therefore, special care is required when reducing the particle size for all of these types of tissues to ensure homogeneity of the prepared sample.

D. Keeping Quality of Plant Tissue

In dealing with large numbers of plant tissue samples, a considerable delay may occur between the time a sample is collected and when it can be decontaminated and oven dried. Therefore, the need to properly store freshly collected tissues to minimize respiratory losses.

Steyn (1959) compared loss in dry weight when fresh citrus leaves were stored in sealed polyethylene bags in the open laboratory atmosphere with that in sealed polyethylene bags put into a freezer set at -5°C . He found that the fresh citrus leaves did not decompose significantly in 1 or 2 d if they are air dried prior to transport to the laboratory (Table 15-7). However, the air-dried leaves were difficult to clean properly to remove surface dust contamination, whereas the fresh leaves stored under refrigerated conditions could be cleaned easily and efficiently. Therefore, if there will be a considerable time lag after sampling and before transport to the laboratory, plant materials are best transferred to the laboratory under refrigerated conditions.

Steyn (1959) has further demonstrated that oven-dried and ground plant material should not be stored on an oven shelf for longer than 8 wk before analysis. On the other hand, this same plant material can be stored indefinitely in a sterilized, sealed bottle in a freezer set at -5°C . The U.S. National Institute of Standards and Technology stores their standard reference plant materials following sterilization by means of gamma radiation in sealed polyethylene bags.

E. Recommended Procedure for the Handling and Preparation of Plant Tissue Samples for Analysis

At each step in the preparative phase, an error made may be manifested in the elemental analysis result. Although any one individual error may not be large, the cumulative effect of several errors may easily result in errors of 10% or more in the final analytical result. Since the whole preparation process is so highly susceptible to error, considerable care is required throughout or the final analytical result will be of little value.

1. Tissues not to be Washed

Place the collected plant tissue in an open-to-the-atmosphere container (e.g., a cotton bag) and transport to the laboratory as quickly as possible. When it arrives at the laboratory, transfer to an oven set at a temperature between 65 and 80°C.

2. Tissue to be Washed

Place the collected plant tissue in a polyethylene bag. If transport to the laboratory is to be the next day, keep the bags containing the tissue under refrigerated conditions. Upon arrival at the laboratory, remove one bag at a time from the refrigerator and wash each tissue sample by sponging with a piece of cotton wool moistened in a 0.1% detergent (Teepol or Dreft) solution, followed by rinsing in two lots of pure water, or in flowing pure water. Place the sample in a clean cotton bag and suspend inside a forced-draft oven set between 65 to 80°C.

3. Grinding and Storage

After drying for 48 h, grind the entire sample to pass a 20-mesh screen or powder in an agate mechanical ball mill. Place the ground or powdered tissue powder in a clean bottle and dry for an additional 24 h at 65°C to remove any moisture added during the particle-size reduction step. After drying, seal the bottle and place it in a cool dry place. For long-term storage, store under refrigerated conditions until the analysis can be done.

F. Alternate Procedure for the Handling of Plant Tissue Samples

Good washing, drying, or refrigeration facilities are not often available on or near the collection site. In this situation, the following is recommended:

- a. Gather the tissue samples as described in Table 15-2, or follow the sampling directions given by the assaying laboratory.
- b. Spread the collected plant sample out in a dust-free area for 1 or 2 d to air dry. This is essential for those types of tissues that have a high water content.
- c. After 1 or 2 d of air drying, place the plant sample loosely in a labeled paper or cloth bag. Avoid packing tightly. Do not put undried plant tissue in plastic bags that will not be refrigerated immediately.
- d. Place the loosely filled paper or cloth bags in a sturdy container, with crumpled newspaper between samples, and transport them to the laboratory as quickly as possible.

Although this sample handling procedure will not enable the laboratory to account properly for contamination from dust or spray residues, the assay procedure will ensure that tissue samples will reach the laboratory in good physical condition.

III. LABORATORY ANALYSIS

There are various assay methods suitable for the determination of the total elemental content of plant tissue. Most involve destruction of the tissue's organic component, thereby converting the elements to a soluble form for analysis. Some have proposed releasing the elements by extracting them from the dried green tissue, but these techniques have been developed for only a few crops and elements, and the procedure is discussed in detail in the next section. Significant analytical advancements have occurred in the last several decades with the introduction of rapid multielement analyzers that use a single prepared sample for the assay of most of the essential elements. These analyzers offer high speed, excellent sensitivity, and precision. In today's analytical laboratory, those having a quality assurance program in force have markedly improved the reliability of obtained analytical results.

A. Methods of Organic Matter Destruction

Probably no other aspect of plant tissue preparation prior to elemental analysis has stirred as much controversy as how best to destroy the organic matter portion of tissue. The best treatises on the subject are the books written by Gorsuch (1970) and Bock (1978) who describe in considerable detail the advantages and difficulties associated with each organic matter destruction procedure. In addition, the review articles by Tolg (1974) and Gorsuch (1976) provide considerable useful information.

There are essentially two decomposition procedures, wet acid digestion and high temperature dry oxidation, frequently referred to as wet and dry ashing, respectively. The appropriate method will depend on elements sought in the analysis, nature of the plant material, difficulty with dissolution, acceptable degree of recovery, required sensitivity, and the capability of a laboratory to manage a particular method as described by Munter et al. (1984).

Wet oxidation is the destruction of organic matter by high temperature acid digestion. The common acids used are H_2SO_4 , HNO_3 , and HClO_4 , usually in some combination of two or all three. Nitric acid is usually included in most digestion mixtures, with the addition of H_2SO_4 to raise the digestion temperature, or the addition of HClO_4 or 30% H_2O_2 to speed and complete the digestion. Tolg (1974) lists the characteristics of various acid mixtures as given in Table 15-8.

Sulfuric acid as a component in the digestion mixture is not recommended when digesting plant tissue high in Ca. Relatively insoluble CaSO_4 may be formed which will lower the Ca determination and possibly other elements by coprecipitation. Lindner and Harley (1942) used hot H_2SO_4 with repeated additions of 30% H_2O_2 until the digestion was complete. Wolf (1982) suggests that this procedure is best suited for small sample aliquots (0.10–0.25 g), and for tissue easily oxidized and relatively low in Cl content. Nitrogen as well as most of the other mineral elements (P, K, Ca, and Mg) can be determined in their digests. Parkinson and Allen (1975) used the H_2SO_4 -30%

Table 15-8. Digestion reagents for use in methods for wet acid oxidation (Tolg, 1974).

Digestion reagents	Applicability to organic matrix	Remarks
H ₂ SO ₄ /HNO ₃	Vegetable origin	The most used; Danger of volatilization of As, Hg, and Se
H ₂ SO ₄ /H ₂ O ₂	Vegetable origin	Pb loss on co-precipitation with CaSO ₄ ; Loss of Ge, As, Ru and Se
HNO ₃	Biological origin	Easily purified reagent; digestion temp. 250°C; short digestion time; soluble metal-nitrates
HClO ₄	Biological origin	Catalyst: (NH ₄) ₂ MoO ₄ , etc.
H ₂ SO ₄ /HClO ₄	Biological origin	Suitable only for small samples; danger of explosion
HNO ₃ /HClO ₄	Protein, carbohydrate (no fat)	Less explosive; no loss of Pb
H ₂ SO ₄ /HNO ₃ /HClO ₄	Universal (also fat and carbon black)	No danger with exact temperature control; As, Sb, Au, and Fe, are volatile, digest under reflux conditions

H₂O₂ mixture plus Se and LiSO₄·H₂O to digest tissue for the determination of N, P, K, Ca, Mg, Cu, Fe, Mn, and Zn. Cresser and Parsons (1979) used a H₂SO₄-HClO₄ digestion mixture for preparing plant tissue for the analysis of N, P, K, Ca, and Mg.

To shorten the digestion time, HClO₄ is added to the digestion mixture. However, HClO₄, when hot, is a strong oxidant that can react with explosive force when brought into contact with easily oxidizable compounds, especially if the digestion mix approaches dryness. Therefore, extreme care is required when using this acid (Horwitz, 1980), and current USA regulations only permit the use of HClO₄ in specially designed fume hoods which continuously wash fumes released in the digestion process.

Today, the wet oxidation procedure is frequently done in digestion tubes inserted into ports of a temperature-controlled digestion block that may be obtained commercially, or constructed by the analyst (Gallaher et al., 1975). With proper control devices, the digestion temperature and time can be carefully controlled, greatly simplifying the digestion procedure. A block-digestion procedure using a mixture of HNO₃ and HClO₄ has been described by Zasoski and Bureau (1977), HClO₄ and H₂O₂ as the digestion mixture by Adler and Wilcox (1985), and a method using HNO₃ alone by Halvin and Soltanpour (1980) and Zarcinas et al. (1987). Huang and Schulte (1985) used a HNO₃-30% H₂O₂ combination for digesting small aliquots of tissue in Folin tubes inserted into a digestion block. Several of these procedures are described in Table 15-9. If a digestion block is not available, most of these procedures can be done in covered beakers placed on a hot plate.

White and Douthit (1985) devised a procedure digesting plant tissue in a mixture of HNO₃ and 30% H₂O₂ heated in a microwave oven, while Ogner (1983) used ultraviolet (UV) radiation as the source of heat. There are several commercial digestion systems that combine microwave heating with sealed digestion vessels for automated rapid wet digestion of plant tissue.

Table 15-9. Acid digestion procedures for organic matter destruction in plant tissue.

Acid digestion procedure (HNO_3 and HClO_4)

Weigh 0.5 g of 20-mesh dried plant tissue into a beaker or digestion tube. Add 2.5 mL conc. HNO_3 . Cover the beaker with watch glass or place funnel into the mouth of digestion tube. Let it stand overnight. Place covered beaker on hot plate or digestion tube into a port of the digestion block. Set the temperature of plate or block at 80°C and digest for 1 h. Remove beaker or digestion tube from plate or block and let cool.

Add 2.5 mL of HClO_4 .

Place covered beaker on hot plate or tube back into digestion block and digest at 180 to 200°C for 2 to 3 h, or until digest is clear. Remove the glass cover from the beaker or funnel from digestion tube and heat at 80°C until fumes of HClO_4 have dissipated. Remove beaker from hot plate or digestion tube from the digestion block and let cool. Add pure water to digest to bring the level to 10 mL.

The digest is ready for elemental assay.

Acid digestion procedure (HNO_3 alone)

Weigh 0.5 g of dried 20-mesh plant tissue into a beaker or digestion tube. Add 5.0 mL conc. HNO_3 . Cover beaker with watch glass or place funnel into the mouth of digestion tube. Let it stand overnight.

Place covered beaker on hot plate or digestion tube into a port of the digestion block.

Set temperature of plate or block at 125°C and digest for 4 h.

Remove beaker from hot plate or digestion tube from the digestion block and let cool.

Add pure water to digest to bring the level to 10 mL.

The digest is ready for elemental assay by ICP-AES only.

Wet digestion procedure (HNO_3 and 30% H_2O_2)

Weigh 0.5 g of dried 20-mesh plant tissue into a beaker or digestion tube. Add 5.0 mL of conc. HNO_3 . Cover beaker with watch glass or place funnel into the mouth of digestion tube. Let it stand overnight.

Place covered beaker on hot plate or digestion tube into a port of the digestion block.

Set temperature of plate or block at 125°C and digest for 1 h. Remove beaker from hot plate or digestion tube from block and let cool.

Repeat cooling and 30% H_2O_2 additions until the digest is clear. Add more HNO_3 as needed to keep digest from going dry.

When the digest is colorless, reduce the temperature of the hotplate or digestion block to 80°C , remove the watch glass from the beaker or funnel from the digestion tube and let the digest go almost to dryness. The residue should be either white or colorless. If not, repeat the higher temperature digestion with additional H_2O_2 treatment. Remove the beaker from the hot plate or digestion tube from the digestion block and let cool.

Add 1:10 (HNO_3) or (HCl) to bring the final volume to 10 mL.

The clear solution is ready for elemental assay.

Wet digestion procedure (H_2SO_4 and 30% H_2O_2)

Weigh 0.5 g of dried 20-mesh plant tissue into a digestion tube. Add 3.5 mL conc. H_2SO_4 and let it stand for 30 min. Add 3.5 mL 30% H_2O_2 .

Place a funnel in the digestion tube, and the tube into a port in the digestion block set at 250°C .

Heat for 30 min. Remove tube from the digestion block and let the tube cool. Add 1 mL 30% H_2O_2 until the digest is clear upon cooling. When clear after cooling, dilute to 20 mL with pure water.

The digest is ready for elemental assay.

All the prepared digest can be directly assayed by ICP-AES, and all but the HNO_3 alone procedure by FIA, without further manipulation.

Sulfate sulfur can be determined for all the acid digested tissue except for that prepared in H_2SO_4 + 30% H_2O_2 .

The mineral elements can be determined in the H_2SO_4 + 30% H_2O_2 digest plus ammonium. Boron is usually determined best in tissue samples prepared by dry ashing.

Wet oxidation under pressure can be performed by placing sample and digestion reagents either into a Parr Bomb (Vigler et al., 1980; Okamoto & Fuwa, 1984), in sealed ampules placed into an autoclave at 125 °C under pressure (Sung et al., 1984; Knapp, 1985; Knapp & Grillo, 1986), or with 6 M HCl at 80 °C in tightly capped polyethylene bottles (Kuennen et al., 1982). These techniques are used for volatile element containment or for tissues difficult to digest completely.

If B is one of the elements to be determined in the plant tissue digest, the dry ash procedure is recommended (Wikner, 1986) since this element can be partially or almost entirely lost by volatilization during wet oxidation (Feldman, 1961). Boron may be retained during wet oxidation for tissue high in Ca. To avoid B additions from the glassware used, the digestion vessels must be heat acid washed and relatively free from scratches.

The critical considerations for organic matter destruction by high temperature oxidation are: (i) the nature of the ashing vessel, (ii) placement in the muffle furnace, (iii) ashing temperature, and (iv) time. Although the shape and size of the ashing vessel is not generally specified, high-walled vessels large enough to keep the sample depth in the vessel minimal are best. A lid on the ashing vessel can minimize loss of ash and contamination from the muffle furnace (Munter et al., 1984), but is not recommended unless a constant flow of air is passed through the muffle furnace. Silica crucibles are one of the best vessels for dry-ashing plant tissue. Pyrex glass high-form beakers and well-glazed porcelain high-form crucibles are also suitable ashing vessels, although the glass beakers may add B and Na to the solubilized ash, and Al from the use of porcelain crucibles.

A critical initial requirement to prevent flaming of tissue in the ashing vessel requires raising the muffle furnace temperature slowly and keeping the furnace door closed. Furnaces with tightly fit doors, or too many ashing vessels placed in the furnace may cause incomplete oxidation due to low O₂ supply.

Keeping the ashing vessel from contact with a heated muffle furnace floor and away from the door is equally important. Frequently, the obtained ash in vessels placed near the furnace door may look darker than those positioned in the center due to less oxidation (caused by cooler temperatures). Therefore, the analyst should determine if vessel position is a factor for the muffle furnace being used, making adjustments as required to ensure even and complete organic matter destruction for every vessel placed in the muffle furnace.

Baker et al. (1964) ashed plant tissues at 458 ± 5 °C for 8 h in a muffle furnace lined with stainless steel which was necessary to eliminate Al and Zn contamination from the walls. Jones and Warner (1969) ashed at 500 °C for 4 h which proved satisfactory for most plant tissues. Cholak and Story (1941) found dry ashing at 500 °C satisfactory for preparing various biological substances without losses of the elements they measured.

According to Gorsuch (1959, 1970, 1976), as long as the ashing temperature does not exceed 500 °C, volatilization losses should not occur for most elements. There is danger from a too low ashing temperature due to incom-

plete organic matter destruction which prevents complete recovery of elements from the organic matrix. Isaac and Jones (1972) ashed plant tissues at temperatures from 400 to 700 °C, and found only the elements Al, B, Cu, Fe, K, and Mn affected by ashing temperature. However, they also observed that when the ashing temperature was 500 °C, the known values for 13 elements (Al, B, Ba, Ca, Cu, Fe, K, Mg, Mn, Mo, P, Sr, and Zn) in a corn leaf tissue standard were obtained. Munter et al. (1984) reported similar results when ashing at the 500 °C temperature, although they emphasized the need for careful temperature control of the muffle furnace. The volatile elements such as As, Cd, Hg, and Pb may be lost during dry ashing, although retention seems to be enhanced for tissues that have high Ca (7.0%) contents.

The length of ashing time necessary to completely oxidize the organic components in plant tissue will vary depending on the type of the tissue. Complete oxidation is more difficult to achieve for tissues high in sugar or oil content. Usually, 4 to 8 h at the ashing temperature is sufficient. If crucible covers (with adequate air-flow in the muffle furnace) are used, an additional 2 h may be needed (Munter et al., 1984) for complete oxidation.

Ashing aids may be used to assist in the decomposition of the plant tissue organic matter, particularly for those tissues high in either sugar or oil content. Gorsuch (1970) recommended 10 mL of 10% H_2SO_4 or 10 mL of 7% $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ per 5-g sample as suitable ashing aids. The AOAC Manual (Horwitz, 1980) procedure for dry ashing calls for HNO_3 as an ashing aid by wetting an obtained ash with dilute HNO_3 acid, taking to dryness and placing in the muffle furnace for another hour. Since the need for an ashing aid is more important for highly carbonaceous tissues, the analyst should experiment with the tissue samples of interest to determine if an aid is needed. If organic matter destruction is complete, then the remaining ash should appear "white" and relatively free from particles of unoxidized C. If a clean white ash is not obtained, then an ashing aid may be needed to assist in the oxidation process.

The procedure used to solubilize the ash may also affect the elemental analysis. The common practice is to dissolve the ash at room temperature in a sufficiently concentrated acid, either HNO_3 or HCl , or a combination of both (aqua regia) to make the final dissolved acid solution 1 *N* in concentration. Acid dissolution at room temperature, however, may not completely release Al, Cr, and Fe (Dalquist & Knoll, 1978). Munter and Grande (1981) suggest adding a weighed aliquot of 2 *N* HCl to the ash, heat on a hot plate until fumes of the acid evolve, let cool, and then bring back to the original weight by the addition of pure water. By this technique, they were able to obtain the certified value for Al and Fe, as well as other elements, using *NIST Plant Tissue Standard Reference Materials (SRMs)*. The *AOAC Manual* (Horwitz, 1980) calls for solubilizing by HCl treatment of the ash on a hot plate. The procedure for ashing and solubilization of the ash is given in Table 15-10.

Complete solubilization of the heavy metal micronutrients, particularly Zn, in plant ash containing sizable quantities of Si (such as rice plant ash), make the dry-ashing technique unsuitable for organic matter destruction

Table 15-10. Organic matter destruction in plant tissue by high temperature oxidation.

Dry ashing procedure

Weigh 0.5 g of dried 20-mesh plant tissue into a 15 mL high form porcelain or quartz crucible.

Place crucible in a rack. Place the rack in a cool muffle furnace. Set furnace temperature to reach set temperature in about 2 h. After 4 to 8 h of muffling at 500 °C, remove the crucible rack from the furnace and let it cool.

Add 10 mL of dilute acid (300 mL of HCl and 100 mL of HNO₃ in 1 L of pure water) to dissolve the ash. Crucible and contents may be heated to assist in dissolving ash by weighing crucible, heating, and bringing back to original weight after cooling. Allow suspended material to settle to the bottom to the crucible.

The clear solution is ready for elemental assay, with or without further dilution.

unless the silica is removed by treating the ash with HF. Therefore, wet digestion is the recommended procedure for high Si-containing tissues.

It has been frequently observed that differences in elemental content will be obtained when the same tissue is either wet digested or dry ashed. The two commonly observed differences occur for the elements Al and Fe (B may or may not be lost during wet ashing). There may be two possible explanations for these differences. Either the insoluble oxides of Al and Fe are formed when dry ashing, and therefore, not brought into solution when the ash is acid solubilized, or during wet ashing, Al and Fe in dust-contaminated tissue are brought into solution. In either case, higher Al and Fe values usually are obtained when tissue is wet digested.

Low-temperature dry ashing is another technique used to retain the more volatile elements (such as As, Hg, and Se) in samples during the destruction of organic matter. Gleit and Holland (1962) introduced the basic procedure, ashing in the presence of electronically excited O₂ (Gleit, 1963). The ashing temperature is from 100 to 150 °C with periods as much as 5 d required to completely destroy the organic matter. Therefore, the procedure is not well suited for high-volume rapid analysis requirements.

In most instances, the method of organic matter destruction is selected on the basis of personal preference without regard as to type of plant material or elements to be determined. It is difficult to find sufficient fault or advantage with either method that would consistently designate one superior to the other. Therefore, the analyst should compare analysis results of plant tissue that has been prepared by both methods of organic matter destruction, and on this basis, choose the method that gives the desired result.

B. Methods of Extraction

Extraction procedures for evaluating the Ca (Gallaher & Jones, 1976); Fe (Machold & Stephen, 1969; Katyal & Sharma, 1980; Chaney, 1984); N and NO₃ (Baker & Smith, 1969); and S and SO₄ (Spencer et al., 1978) status of plants have been proposed. Grunau and Swiader (1986) used ion chromatography to measure the Cl, NO₃, SO₄, and PO₄ in water extracts of several dried vegetable leaves, with good results reported except for PO₄. Ulrich et al. (1959) used 2% acetic acid to extract P and K from sugarbeet

Table 15-11. Extraction procedure for NO_3 in plant tissue.

<u>Baker and Smith (1969) method</u>	
1.	Weigh 400 mg of oven-dried ground (80°C, 20-mesh) tissue into shaking bottle.
2.	Add 40 mL extracting solution [0.025 M $\text{Al}_2(\text{SO}_4)_3$ containing 10 $\mu\text{g mL}^{-1}$ $\text{NO}_3\text{-N}$ and 1 mL L^{-1} preservation].
3.	Shake for 15 min.
4.	Filter and save filtrate for $\text{NO}_3\text{-N}$ assay.
<u>Heanes (1982) method</u>	
1.	Weigh 400 mg of oven-dried ground (80°C, 20-mesh) tissue into shaking bottle.
2.	Add 50 mg of oxidized activated charcoal (AC).
3.	Add 40 mL 0.025 M $\text{Al}_2(\text{SO}_4)_3$.
4.	Shake for 30 min.
5.	Filter into shaking bottle containing 500 mg of oxidized AC.
6.	Shake filtrate plus AC for 30 min.
7.	Filter and save filtrate for $\text{NO}_3\text{-N}$ assay.

(*Beta vulgaris* L.) petioles. Sahrawat (1980, 1987), Hunt (1982), and Miyazawa et al. (1984) used dilute HCl as an extraction reagent to determine Ca, Mg, K, Mn, Cu, Zn, Fe, and P content in dried plant tissue. Baker and Greweling (1967) developed an extraction procedure that gave results comparable to those for dry-ashed samples for the elements Ca, Mg, K, Mn, Cu, and Zn. Nicholas (1957) also obtained good correlations between results obtained by extraction with total for the elements Ca, K, Mn, and P. The determination of B by extraction using HCl-HF has been suggested by van der Lee et al. (1987).

The most frequent chemical form obtained by extraction is $\text{NO}_3\text{-N}$. A widely used method of extraction first described by Baker and Smith (1969) and then modified by Heanes (1982) is given in Table 15-11. Mills (1980) suggests water as a satisfactory extraction reagent. A good review of the techniques and procedures for extraction and determination of $\text{NO}_3\text{-N}$ has been written by Keeney and Nelson (1982).

All of these extraction procedures are laboratory conducted tests using oven-dried and milled tissue, and should not be confused with procedures called *tissue-tests*, tests conducted in the field on extracted sap from fresh tissue. Tissue testing will be discussed in another section of this chapter.

C. Methods of Elemental Determination

Advances in analytical chemistry since 1970 have significantly improved the ease and speed for the determination of elements found in plant tissue ash or digests. For most of the elements, frequently referred to as the *mineral elements*, the more traditional wet chemistry procedures have given way to various instrumental procedures that employ either emission or absorption spectrometry.

The classical colorimetric procedures have been described in detail by Piper (1942), Jackson (1958), Johnson and Ulrich (1959), Greweling (1976), and Chapman and Pratt (1982). The last two references describe flame emission and atomic absorption spectrometry procedures as well. Many of these

colorimetric and flame emission procedures have been automated by employing an AutoAnalyzer® as described by Isaac and Jones (1970), and Steckel and Flannery (1971) for the determination of Ca, K, Mg, and P, and for B as described by Basson et al. (1969). Some of these same colorimetric procedures can be employed using automated flow injection analysis (Ranger, 1981).

Flame emission spectrometry for the determination of K and Na (Marrodineanu, 1970) as well as Cu, Fe, and Mn (Berneking & Schrenk, 1957; Pickett & Koirtzohann, 1969; Keliher et al., 1984), and atomic absorption spectrometry (whose acronym is AA) for the determination of Ca, Mg, Cu, Fe, Mn, and Zn are procedures that have been described by Greweling (1976), and in review articles by Isaac and Kerber (1971), Isaac (1980), Baker and Suhr (1982), and Ure (1983), and the book by Christian and Feldman (1970). Although both instrumental methods are still in wide use today, they are slow and cumbersome when compared to the more recently developed spectrometer techniques. Having a narrow dynamic reading range of up to two decades, considerable sample manipulation may be required to bring elemental concentrations within the calibration range of the spectrometer. In addition, only one element at a time can be determined.

Direct reading emission spectrometry, using a progression of excitation sources from AC and DC arcs (Cholak & Story, 1941; Mitchell, 1956, 1964; Thompson & Bankston, 1969), AC spark (Jones, 1976), the inductively coupled plasma (Jones, 1977; Dalquist & Knoll, 1978; Munter & Grande, 1981; Soltanpour et al., 1982; Zarcinas, 1984; Zarcinas et al. (1987), and the DC plasma (DeBolt, 1980), has been a major analytical technique for the assay of most elements found in plant tissue ash or digests. With one pass of the prepared sample through the excitation source, most of the plant essential elements (P, K, Ca, Mg, B, Cu, Fe, Mn, and Zn, and S for vacuum spectrometers) as well as nonessential elements (Al, As, Cd, Co, Cr, Ni, Pb, and Se) can be determined either simultaneously, in < 60 s, or sequentially in < 120 to 180 s. Plasma spectrometry is also relatively free from matrix and spectral interferences, has excellent sensitivity (usually < 1 mg/kg) and a wide concentration reading range of several decades (between three to five). Inductively coupled agron plasma emission spectrometry is frequently referred to by its acronym, ICP or ICAP. There are two recent books on ICP, one by Walsh (1983) and the other edited by Montaser and Golightly (1987).

The spectrometer receiving and recording an ICP generated emission can have either an air or vacuum light path. Evacuated spectrometers can detect emission lines in the UV region of the spectrum (most useful for the elements B, P, and S). The spectrometer design may be either a sequential monochromator which records one emission line at a time, or a polychromator that has a detector for each element so that elemental determinations are made simultaneously (Nygaard & Sofera, 1988).

Sample preparation is relatively simple. First the organic matter is destroyed, and then the dissolved ash or digest solution is directly introduced into the ICP. This is in marked contrast to the more traditional wet chemical procedures and other single element analyzers that require considerable

manipulation of the plant ash or digest solution prior to the determination of its elemental content. Since these latter procedures require substantial amounts of effort and time to perform an analysis, they are costly and subject to potential errors.

Another method of elemental determination in plant tissue has been x-ray fluorescence, procedures that have been described by Dixon and Wear (1964), Alexander (1965), Jenkins and Hurley (1966), Kubota and Lazar (1971), Murray (1975), and Jones (1982). However, the method is strongly affected by the matrix influences and is not a widely used technique for plant analysis.

It is difficult to specifically select any one method or technique as superior to another. There have been various studies conducted that have tried to make this distinction (Kenworthy et al., 1956; Bowen, 1967; Brech, 1968; Jones, 1969; Jones & Isaac, 1969). Others have studied the variance associated with various methods of analysis (Baker et al., 1964; Carpenter et al., 1968; Jones & Warner, 1969; Munter et al., 1984). However, the emphasis today is on quality assurance and performance testing as the means of assuring reliable performance for the analytical procedure used, laboratory management procedures that are discussed in more detail later. Unfortunately in most instances, method selection is based on what instrumentation and facilities are available, rather than a decision based on best method for the element(s) determined and form of the matrix.

1. Nitrogen

Total and approximate total N in plant tissue can be determined by essentially two analytical procedures. The Dumas (Bremner & Tabatabai, 1971; Edeling, 1968) technique for total N involves the conversion of organic N to molecular N. Although automated Dumas instruments are readily available, such as the LECO FP-228 (Sweeney & Rexroad, 1987) and are fairly easy to use, their high cost and low analytical capacity (< 10 samples/h) limits their use for routine analytical purposes. In addition, since usually < 100 mg samples are assayed, the plant tissue must be finely ground to obtain a reasonably homogenous sample. Nitrogen content determination by the Dumas procedure as compared to that obtained by Kjeldahl digestion, the most widely used N determination method, usually gives slightly (1–4%) higher results.

The original Kjeldahl digestion procedure was developed by Johan Kjeldahl in Denmark in the late 1800s. The first published procedure appeared in 1883 (Morries, 1983), making it the oldest analytical method still in use today. The method is in two steps; first, high temperature (330–450 °C) digestion in concentrated H_2SO_4 in the presence of a catalyst (Cu, Hg, or Se, or the combination of Cu-TiO₂) which converts organic N to inorganic NH_4 , which combines with SO_4 to form $(\text{NH}_4)_2\text{SO}_4$; and the second step, either alkaline distillation of NH_3 and determination of NH_4 by acidimetric titration (Munsinger & McKinney, 1982), or determination of NH_4 by a colorimetric procedure (Warner & Jones, 1970; Crooke & Simpson, 1971; Uhl et al., 1971; Isaac & Johnson, 1976; Smith, 1980; Wang & Oien, 1986),

or NH_4 determination by specific ion electrode (Gallaher et al., 1976). Numerous procedures have been proposed on how to conduct the Kjeldahl digestion step designed to simplify it as well as improve precision and accuracy. Nelson and Sommers (1980) have reviewed and evaluated many of the various modifications proposed for the Kjeldahl procedure as well as the NH_4 determination.

Depending on sample size, the Kjeldahl digestion procedure has been classed as being either macro- (1.0 g or greater), semimicro- (1.0–0.5 g), micro- (< 0.5 g), with the size of the digestion/distillation apparatus scaled accordingly. Precision declines with decreasing sample size (< 0.5 g) due to the lack of homogeneity among plant tissue particles, and, therefore, the need for a more finely ground sample (< 20 mesh) to ensure adequate homogeneity (Batey et al., 1974). The trend from macro- to micro-Kjeldahl digestion is an attempt to reduce the required laboratory space and equipment needed as well as to reduce reagent use (Campbell, 1986).

Today, the digestion block, which can be either constructed by the analyst (Gallaher et al., 1975) or obtained commercially seems to be the procedure of choice (Munsinger & McKinney, 1982). The digestion is carried out in a digestion tube set in the heated block, with tube size dictated by sample size (Nelson & Sommers, 1973; Noel & Hambleton, 1976). The NH_4 formed is determined by titration after being volatilized by steam distillation into a trapping solution (Campbell, 1986). There is also a fully automated Kjeldahl apparatus which is in fairly wide use (Anonymous, 1980).

Nitrogen in plant tissue as either NO_3 or NO_2 is not completely recovered in the Kjeldahl digestion unless converted to NH_4 by pretreatment of the sample with either reduced Fe under acidic conditions (Cataldo et al., 1974) or pretreatment in a moisture-free environment with salicylic acid or thiosulfate (Dalal et al., 1984). The Kjeldahl procedure, with and without NO_3 or NO_2 recovery, and NH_4 determination by alkaline distillation is given in the AOAC Manual under "Fertilizers" (Horwitz, 1980). Data from Whitehead and Olson (1942) suggest that some of the NO_3 in plant material is reduced and included in the Kjeldahl procedure that does not normally include NO_3 in inorganic fertilizer materials. These researchers added 4.2 to 16.6 mg of $\text{NO}_3\text{-N}$ as KNO_3 solution to varying aliquots (0.5–2.0 g) of oat (*Avena sativa* L.) straw that contained 3.3 to 13.3 mg of N based on Kjeldahl method without added reducing agents. About 40% to more than 70% of the added $\text{NO}_3\text{-N}$ was recovered. The amount of NO_3 added and type of catalyst had more of an effect than amount of sample used.

Some have used either HClO_4 (Batey et al., 1974) or 30% H_2O_2 (Lindner & Harley, 1942; Wolf, 1982; Parkinson & Allen, 1975) in place of a catalyst so that the obtained digest can be used for N determination as well as other elements, such as P, K, Ca, and Mg plus the micronutrients. However, Nelson and Sommers (1973) found that H_2O_2 additions can reduce N recoveries by about 15%.

The addition of either K_2SO_4 or Na_2SO_4 , but mostly K_2SO_4 , to the digestion mixture will increase the temperature of the digestion from 330°C with pure H_2SO_4 to 350°C, or higher, which in turn speeds the digestion

Table 15-12. Standard Kjeldahl digestion procedure (for determination in Kjeldahl flask or digestion tube).

Weigh 500 mg of dried ground plant tissue (80°C and 40 mesh) into a Kjeldahl flask or digestion tube.
 Add 5.0 g of digestion mixture [100:1:1000 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}:\text{Se}:\text{K}_2\text{SO}_4$], or [1:60:1670:(CuSO_4): $\text{TiO}_2:\text{K}_2\text{SO}_4$].
 Add 10 mL conc. H_2SO_4 .
 Place Kjeldahl flask on digestion rack, or place funnel in the neck of the digestion tube and place the tube into a port of the digestion block. Heat to rolling boil in Kjeldahl flask or at 360 to 410°C for digestion block.
 Continue to heat for 60 min after clearing.
 Discontinue heating and let Kjeldahl flask or digestion tube and contents cool.
 Dilute to appropriate volume with pure water and determine NH_4 content in digest.

time and increases N recovered. The amount of either sulfate salt added to the acid is 0.3 to 0.5 g/mL of H_2SO_4 . If the addition of K_2SO_4 to the digestion mixture results in solidification during the digestion step, some N will be lost by volatilization.

Either Cu or Hg, or Se alone, or the combination Cu-TiO₂ (Kane, 1986, 1987) have been used as catalysts in the Kjeldahl digestion procedure. Mercury is the catalyst most frequently specified for the N determination in plant tissue and is the one recommended in the official AOAC procedure (Horwitz, 1980) as well as that given by the American Association of Cereal Chemists (Christensen, 1983). If Hg is the catalyst selected, then S_2O_3 must be added to the digest in the distillation step to break the Hg-NH₄ complex that is formed. Mercury as well as Se are elements of concern today due to their potential health hazard. Therefore, their recommended use as catalysts has been discouraged and replaced by either Cu (Rexroad & Cathey, 1976) or Cu-TiO₂ (Kane, 1986, 1987).

Digestion time is an important consideration for the complete conversion of organic N to NH₄ to occur. When the digestion mixture clears, an additional period of two to three times that required for clearing is needed to obtain near complete conversion of organic N to NH₄. At clearing, about 90 to 92% of the organic N in most plant samples has been converted with the additional digestion time needed to obtain most of the remaining 7 to 8% N.

The determination of N in plant tissue by Kjeldahl digestion gives something less than total N content. Therefore, the use of the word "Kjeldahl" to designate "Total N" is not correct. Also, the word Kjeldahl is not sufficient to be used alone without some explanation of how the analysis was performed in terms of sample size, apparatus, and catalyst used as well as whether NO₃ was recovered (Jones, 1987). A generic description of the Kjeldahl digestion step is given in Table 15-12. Verification of the Kjeldahl N determination is important as recommended by Hach and Brayton (1985).

Currently, there are several non-Kjeldahl methods for N determination in plant tissue that are being investigated. One method is by direct distillation, placing a plant tissue sample into alkali and steam distilling for a specified time (Anonymous, 1981). The amount of amino-N converted to NH₄ and measured is compared with a predetermined Kjeldahl N value by means

of a calibration curve. An essential requirement for the procedure is precise control of the distillation time and temperature if reliable results are to be obtained.

Another is a chemiluminescent N system based on the conversion of bound N to NO which is converted to NO₂ in the presence of ozone (Anonymous, 1982). Jacques and Peterson (1987) found the technique has excellent sensitivity, but precision is significantly affected by sample size and the combustion boat design.

Near infrared reflectance (NIR) is the procedure that looks promising for determination of plant N (Dorsheimer & Isaac, 1982; Mundel & Schaalje, 1988). A beam of infrared radiation is focused on a finely ground dried plant tissue sample and the reflected radiation measured. The technique is fast and nondestructive; however, the instrument is expensive and the calibration procedure requires the use of standards of the same plant species as those to be assayed. Isaac and Johnson (1983) compared N determinations in corn leaves obtained by NIR with that obtained by Kjeldahl digestion, a comparison they described as quite good, but not sufficient to recommend the NIR technique. However, Blakeney et al. (1988) obtained agreement between N determined by NIR and Kjeldahl digestion using whole rice (*Oryza sativa* L.) stem samples finely ground in a cyclone mill.

Sulfur

Total S in plants can be determined by several techniques with comparable results. One procedure follows wet oxidation of a plant tissue sample in a mixture of HNO₃ and HClO₄, converting organic S to SO₄-S. The SO₄ content in the digest is then determined by either the BaSO₄ turbidity method or by one of several colorimetric procedures (Beaton et al., 1968). The BaSO₄ turbidity method has been adapted for use with an Auto-Analyzer® (Wall et al. 1980).

Automated combustion using a Leco Sulfur Analyzer is another method for determining total plant S. A prepared plant tissue sample is placed into the induction furnace of the analyzer and heated to 1350 °C in a stream of O₂. Plant S is oxidized to SO₂ which is either trapped in an indicator solution and the amount of SO₂ evolved determined by a back titration (Jones & Issac, 1972), or the SO₂ is passed through an infrared analyzer (Hern, 1984). The titration technique requires removing interfering Cl and N prior to S analysis which is done by mixing MgO with the plant tissue and ashing at 500 °C for 2 h.

Sulfur can also be determined by x-ray emission spectrometry (Alexander, 1965; Kubota & Lazar, 1971; Murdock & Murdock, 1977) using a dried ground plant tissue sample. The analysis technique is relatively easy since little sample preparation is required, but the method does require the use of an expensive analytical instrument. In addition to S, several other elements can be determined by this instrumental procedure (Maclauchlan et al., 1987), a method that is sensitive to the physical and chemical characteristics of the sample itself. Although x-ray emission spectrometry has had

a fairly long history of use, it has not been widely used as a major instrumental procedure for routine assay of plant tissue for its elemental content.

D. Quality Assurance

Quality assurance in an analytical laboratory is an important management tool which is designed to ensure reliable performance, and is becoming a national policy for many types of testing laboratories (Aldehnoff & Ernest, 1983). Criteria for implementation have been established by the Association of Official Analytical Chemists (Garfield, 1984). The elements of a quality assurance program are: (i) administration, (ii) personnel management, (iii) management of equipment and supplies, (iv) records maintenance, (v) sample analysis, (vi) proficiency testing, (vii) audit procedures, and (viii) design and safety of facilities. Application of quality assurance criteria on an actual analytical procedure are discussed in detail in the books by Dux (1986) and Taylor (1987).

The basis for reliable performance in an analytical laboratory has been titled "Good Laboratory Practices," the subject of a *Federal Register* entry in 1979 (Anonymous, 1979), and is described in some detail by Fischbeck (1980). The Council of Independent Laboratories (Anonymous, 1976), the Environmental Protection Agency (Booth, 1979), and the National Bureau of Standards (Berman, 1980) have recently published proceedings of symposia on the subject of laboratory performance.

Horwitz (1982), based on his many years of association with the Association of Official Analytical Chemists, has discussed the practical limits of acceptable variability for methods of analysis, focusing on the important aspects of reliability, reproducibility, repeatability, systematic error of bias, specificity, and limit of reliable measurement. The impact of these aspects on any analytical procedure varies considerably in terms of sample size, determinations made, concentrations of the analyte, and the characteristics of analytical instrument used. An additional criteria is the ruggedness factor that sets the limits for each step in the analytical procedure, and when exceeded, will invalidate the obtained results. Examples would be how much variation in temperature or time could be tolerated for a given procedure without a significant change in the result occurring, thereby making the obtained result invalid. Unfortunately, most plant analysis procedures have not been so described. Examples would be limit criteria for sample preparation procedures such as moisture removal criteria, ashing and digestion temperatures, and length of time; and procedures described earlier in this chapter but without carefully defined limits in some instances.

The analyst today has a wide range of instrumentation from which to choose. Some of the factors that affect the choice made are described by McLaughlin et al. (1979). A similar evaluation of analytical technique has been developed by Hislop (1980) as shown in Table 15-13.

Practical considerations, such as instrument availability, and its purchase price and operating cost frequently are governing factors that determine the choice of analytical procedure rather than Hislop's criteria. In

Table 15-13. Analytical criteria for selecting technique of analysis (Hislop, 1980).

Accuracy	Elemental coverage
Precision	Single or multielement
Limit of detection	Determine chemical form

addition, the skill and experience of the analyst may also govern the selection of a particular method or instrument. Those in search of a suitable analytical procedure may find the articles by Morrison (1979) and Stika and Morrison (1981) useful as they compare the relative sensitivity and precision of various methods. For many of the elements, sensitivity is not a significant factor when assaying a plant tissue digest or plant ash for its elemental content since many elemental contents are quite high. Therefore, the choice of analytical procedure could then be based on precision alone. This suggests that different instrument techniques may have to be selected depending on the needs in terms of sensitivity and precision requirements.

The issues of sensitivity, precision, and accuracy are important considerations for the analyst and should be significant determining factors in method selection. Sensitivity has been variously defined as two parameters, the minimum level of detectability, and the ability to significantly distinguish between two analytical values. The detection limit is the smallest concentration that can be identified as being greater than zero and is usually defined as either 2 or 3 SD above a background determination. Sensitivity in terms of level distinction is confounded with precision.

Precision is a measure of the degree of variability associated with an obtained analytical result that is determined by repeated assays of the same sample carried through all the steps from sample preparation to the final result. Poor precision may be the compounded result of accumulated errors made over the entire analytical procedure, and therefore, not the result of a single factor. Hislop (1980) has written an excellent article on the requirements for obtaining accurate and precise analytical results. Horwitz (1982) also has evaluated various analytical procedures by assigning levels of performance by analytical technique, basing this judgment on years of experience in the determination of elements and substances in various materials. Dux (1986) describes how precision determinations can be made a part of a quality assurance program.

Accuracy is the ability of the method to obtain the "true" value and is dependent on the use of reliable standards and matrix matching. Several kinds of standards are needed in the laboratory, one set to monitor analytical procedures, and another set to calibrate instruments and standardize reagents. Prepared and certified standard solutions and reagents can be obtained from many chemical supply houses. Standard References Materials (Uriano, 1979) are available from the U.S. National Institute for Standards and Technology (Alvarez, 1980). Currently, there are four plant tissues (tomato leaves, citrus leaves, pine needles, and spinach), and one animal tissue (bovine liver) available as SRMs. Unfortunately, not every element of interest to the plant nutritionist is certified in all these SRMs, which does limit

their usefulness. However, SRMs should be used when ever possible for verification of accuracy as outlined in the handbook for SRM users (Taylor, 1985).

In the normal laboratory routine, a standard can be used not only to monitor an analytical procedure, but when placed into a sequence of unknowns, it serves the dual purpose as marker and standard. By noting the position and value of the marker-standard at the end of an analytical run, the analyst can determine if an unknown had been skipped or duplicated as well as evaluating if a shift in the calibration has occurred. An evaluated calibration shift may then become the basis for adjustment for results obtained between each marker-standard.

These factors and others form the basis for an established quality assurance program as has been defined by Garfield (1984), Dux (1986), and Taylor (1987). Without such a program of laboratory and analytical management, performance in terms of reliable analytical results cannot be obtained. A recent study reported by Munter et al. (1984) points to certain areas of concern when conducting an elemental assay of plant tissue. They found that both preparation procedures and instrument calibration techniques should be standardized to minimize variation. A similar study by Sterrett et al. (1987) uncovered errors in the determination for various elements in plant tissue. Both these papers point to the need for careful evaluation of each step in the analytical process on the basis of quality assurance parameters.

IV. TISSUE TESTING

A distinction is made between plant (leaf) analysis and tissue testing. The former is a laboratory analysis on dried and ground plant tissue sample, while a tissue test is an assessment of the elemental content of sap taken from fresh tissue with procedures that are usually carried out in the field using special testing techniques.

Krantz et al. (1948) give instructions for the field testing of corn (*Zea mays* L.), and cotton (*Gossypium hirsutum* L.), and soybean [*Glycine max* (L.) Merr.] plants using sap pressed from fresh tissue for the semiquantitative determination for the ions NO_3^- , PO_4^{3-} , and K^+ . Wickstrom (1967) has also written procedures that use such tissue tests for field diagnosis. Syltje et al. (1972) have given procedural details for field-conducted tissue tests on corn and soybean for the elements N, P, Mg, and Mn. They give instructions for preparation of the reagents as well as a description of techniques for conducting the tests. Scaife and Stevens (1983) have found the use of "Merckoquant" test strips suitable for NO_3^- determination in the field assessment of the N status of various vegetable crops.

Iron is an element that can be determined by a tissue test conducted in the field, a procedure first developed by Bar-Akiva et al. (1978) and modified by Bar-Akiva (1984). Peroxidase activity is measured by floating leaf discs in a reactive solution with the development of a blue color indicating adequate Fe in the plant tissue.

The ability to perform tissue tests in the field is considered by some to be a significant advantage in terms of immediate test results and low cost compared to that required for a laboratory conducted plant analysis. It should be remembered that most of the tests themselves are not entirely quantitative, but provide the tester with a qualitative "yes or no" evaluation; that is, the element or chemical form is either present or not present at the desired concentration level. Considerable practical experience using these test procedures and repeated observations are required before one can feel confident when making an interpretation based on such a test result. Tissue tests and their interpretation are considered by some to be more of an "art" than a strict quantitative analytical science. However, it should be remembered that the test procedures themselves are based on sound analytical chemistry, but their utilization and interpretation requires skill that can be gained only by repeated practical experience. Combining field observations with soil and plant tissue quick test procedures has been coined "The Diagnostic Approach," a procedure of observation, testing, and evaluation that has been discussed in detail in a special issue of *Better Crops* (Armstrong, 1984).

V. SUMMARY

Considerable care is required when sampling, handling, and assaying plant tissue if a plant analysis is to be a useful diagnostic tool. Failure to follow prescribed procedures anywhere in the process can lead to erroneous results, and then, faulty conclusions. Sampling may still be the weakest link in the plant analysis technique, and those who collect plant tissue samples must be properly instructed and trained. Although improvements in various aspects of the plant analysis technique are still needed, the procedures for proper cleaning, drying, milling, and storing plant tissue have been fairly well established. By using multielement analytical instruments, such as ICP emission spectrometer, or the flow injection analyzer (FIA), an analyst can quickly and easily assay a plant ash or digest for most of the essential elements. Analytically, there is need to standardize the Kjeldahl digestion procedure that will accurately define the N forms included. Analysts should be using known plant tissue standards such as SRMs from the U.S. National Institute of Standards and Technology or other similar sources for instrument calibration and accuracy assessment. Laboratories should have a quality assurance program in force that follows the current guidelines established by the Association of Official Analytical Chemists.

If the collection, preparation, and elemental determination is done properly, then the plant analysis result can effectively evaluate the nutrient status of the plant. The analysis result can either be used to identify suspected elemental deficiencies, serve to monitor the soil/plant nutrient element status, or provide the basis for formulating lime and fertilizer treatments necessary to ensure high yield and quality.

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Chapter 16

Plant Analysis as an Aid in Fertilizing Sugarbeet

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Plant analysis, in its simplest terms, is a study of the relationship of the nutrient content of plants to their growth. Through research and experience, reference concentrations of mineral nutrients in specific plant parts are determined and used as guides to indicate how well plants are supplied with these nutrients at a certain time of sampling. Such reference concentrations provide a tool to assist the agronomist in evaluating nutrient disorders and improving fertilizing practices.

A basic concept of plant analysis is that the concentration of a nutrient within the plant at any particular moment is an integrated value resulting from all the growth factors that have influenced the concentration up to the time of sampling. This is a straightforward diagnostic procedure as the plant is “asked” about its nutrient problems rather than using the indirect approach of soil analysis to interpret plant growth.

Research and practical experience show that plant analysis can serve as an effective guide in the fertilization of sugarbeet (*Beta vulgaris* L.) (Ulrich, 1948a, b; Ririe et al., 1954; Hills et al., 1982). This summary presents the concepts important to the use of plant analysis and suggests ways of using it to improve the management of sugarbeet fertilization. Practically, plant analysis in sugarbeet culture is most useful in controlling the use of N fertilizer to provide sufficient N early in the growing season to develop large roots (storage roots) followed by N depletion prior to harvest to obtain roots high in sucrose concentration and low in N compounds harmful to the recovery of sucrose in processing. This procedure optimizes net income for the grower and processor and minimizes the pollution of groundwater by leaching nitrates.

I. THE CRITICAL CONCENTRATION

A. Estimation

The critical concentration is a useful reference point in using plant analysis as a tool for determining the nutrient status of sugarbeet plants. It is defined, for a given form of nutrient and specific plant part, as the concentration at which the growth rate of the plant begins to decline significantly. It is best estimated through the use of solution culture but soil pot culture or field experiments have also been used (Ulrich, 1950, 1952). Solution culture has the advantage of permitting the addition of a nutrient in quantitative doses so that some plants at harvest can be simultaneously extremely deficient, mildly deficient, and amply supplied with the nutrient being studied. The responses of plants to nutrient additions are largely independent of their source, and it makes little difference to the plant whether its roots are in culture solution or in a soil. The symptoms and nutrient concentrations of the affected leaves are for all practical purposes identical in both growth media. It follows that the critical value or values associated with deficiency symptoms have nearly universal application (Ulrich, 1948a; Table 16-1).

In each nutrient calibration, a series of plants in pots is supplied with increasing amounts of the nutrient under study, maintaining all other nutrients at adequate levels (Ulrich, 1950; Rosell & Ulrich, 1964). In such a series only one nutrient should be limiting growth at a time, otherwise, if a second nutrient becomes deficient, the concentration of the first nutrient will increase greatly and lead to an erroneous estimate of its critical concentration.

Plants are leaf-sampled and harvested when the lower one-third or one-half of the nutrient series show deficiency symptoms (Fig. 16-1). A calibration curve is then constructed, relating nutrient concentration in a specific plant part to growth, with growth usually expressed as a percentage of the treatments giving maximum growth. A schematic diagram of a calibration curve involving four zones is shown in Fig. 16-2. In the first of these zones, the zone of deficiency, plant growth increases sharply as more nutrient is absorbed, but there is little change in the concentration of the nutrient in the plant part analyzed. Within the second zone, the transition zone, both nutrient concentration and growth increase as more nutrient is absorbed. The third, or adequate zone, is that region of the curve where each addition of the nutrient raises the nutrient concentration without a corresponding increase in growth. The fourth zone, the toxic zone, is where growth decreases as nutrient concentration increases.

The critical concentration lies within the transition zone and is associated with a reduction in growth, usually 10%, or the breaking point of the curve, or the midpoint of the transition zone. The critical concentration will differ somewhat depending on which growth criterion is used and the magnitude of the nutrient concentration range within the transition zone. The most useful calibration curve is the one in which the range in values from deficiency to adequacy is large and the transition zone is sharp, i.e., there is a narrow range in nutrient concentration between plants that are deficient

Table 16-1. A plant analysis guide for sugarbeet.

Nutrient	Plant part	Concentration of element†		
		Critical value field samples‡§	Range showing deficiency symptoms¶	Range without deficiency symptoms#
Boron	Blade	21	12-40	35-200
Calcium	Petiole	1 g/kg	0.4-10 g/kg	2-25 g/kg
	Blade	5 g/kg	1-4 g/kg	4-15 g/kg
Chlorine	Petiole	4 g/kg	0.1-0.4 g/kg	8-85 g/kg
Copper	Blade	--	< 2	< 2
Iron	Blade	55	20-55	60-140
	Petiole	--	0.1-0.3 g/kg	1-7 g/kg
Magnesium	Blade	--	0.25-0.5 g/kg	1-25 g/kg
	Blade	10	4-20	25-360
Manganese	Blade	--	0.01-0.15	0.20-20.0
Molybdenum	Petiole	1 000	70-500	350-35 000
Nitrogen (NO ₃ ⁻ -N)	Storage root	1 000	70-500	800-4 000
	Petiole	750	150-400	750-4 000
Phosphorus (H ₂ PO ₄ ⁻ -P)	Blade	--	250-700	1 000-8 000
	Seedling:			
	Petiole	1 500	500-1 300	1 600-5 000
	Blade	3 000	500-1 700	3 500-14 000
	Cotyledon	1 500	200-700	1 600-13 000
Potassium (Na > 1.5%)	Petiole	10 g/kg	2-6 g/kg	10-110 g/kg
	Blade	10 g/kg	3-6 g/kg	10-60 g/kg
Potassium (Na < 1.5%)	Petiole††	--	5-20 g/kg	25-90 g/kg
	Blade	10 g/kg	4-5 g/kg	10-60 g/kg
Sodium	Petiole	--	--	0.2-90 g/kg
	Blade	--	--	0.2-37 g/kg
Sulfur (SO ₄ ²⁻ -S)	Blade	250	50-200	500-14 000
Zinc	Blade	9	2-13	10-80

† All concentrations are for the element on a dry wt. basis and are mg/kg (ppm), except when noted as g/kg [Note, (g/kg)10⁻¹ = %].

‡ The critical concentration is that nutrient concentration at which plant growth begins to decrease in comparison with plants above the critical concentration.

§ All critical concentrations except for P in seedlings and for N in roots are based on a sample of leaves that have just fully expanded (Fig. 16-3).

¶ Leaf material for chemical analysis must be collected shortly after appearance of leaf symptoms, otherwise deficient plants may accumulate nutrients in the leaf without restoring chlorotic tissues to normal. Use a color atlas (Ulrich & Hills, 1969) to help identify what deficiency, if any, has occurred.

The upper value reported is the highest value observed to date for normal plants. Abnormally high values are often associated with other nutrient deficiencies; for example, blades low in Fe may contain up to 40 g of Ca/kg.

†† Because of the influence of Na on K content of petioles, blades must be used for K analysis when petioles contain < 15 g of Na/kg.

and those that are just well supplied with the nutrient in question. When the transition zone is sharp, any of the above criteria for establishing the critical concentration will lead to essentially the same value.

Calibration curves can be constructed for nutrient concentrations in various parts of a plant (petioles and blades of leaves of different ages, roots, and midstems) and for various forms of a nutrient (e.g., total N, NO₃⁻-N, total P, and soluble H₂PO₄⁻-P). The plant part selected to serve as a reliable indicator of nutrient status should give comparable results for all sam-

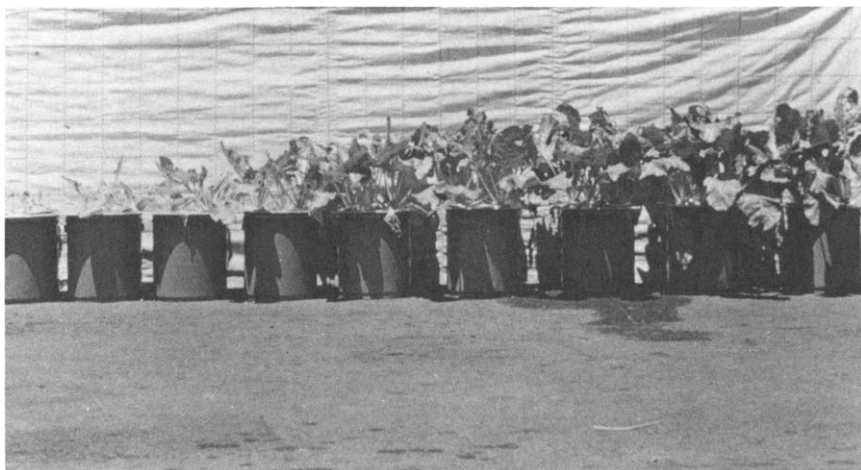


Fig. 16-1. Sugarbeet plants growing in culture solution to which increasing amounts of Zn were added (Rosell & Ulrich, 1964). To establish a calibration curve (Fig. 16-2) plants must be harvested when there are wide differences in growth and nutrient concentration.

pling dates and should be relatively easy to sample. The form of the nutrient determined should result in a calibration curve with a relatively sharp transition zone, a broad range in nutrient concentration between deficiency and abundance, and a relatively constant critical concentration for a considerable range of sampling dates. Sugarbeet leaves usually are the most appropriate part to sample. Sharper calibration curves are usually obtained with recently matured leaves, i.e., leaves that have just attained maximum size (Fig. 16-3) and with mobile rather than nonmobile forms of a nutrient. The petiole has been found to be most satisfactory for NO_3^- -N, H_2PO_4^- -P, and Cl^- , while the blade is more satisfactory for SO_4^{2-} -S and the other essential nutrients.

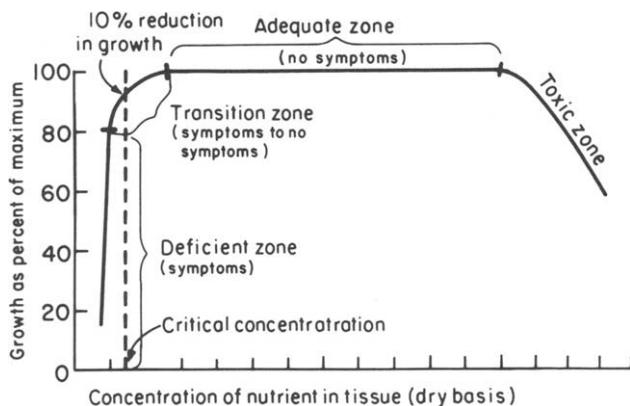


Fig. 16-2. The critical concentration is taken at the point where growth is 10% less than the maximum. Symptoms generally appear below the critical concentration and fail to appear above it. Symptoms may or may not appear in the transition zone. The sharper the transition zone, the more useful the calibration for diagnostic purposes.

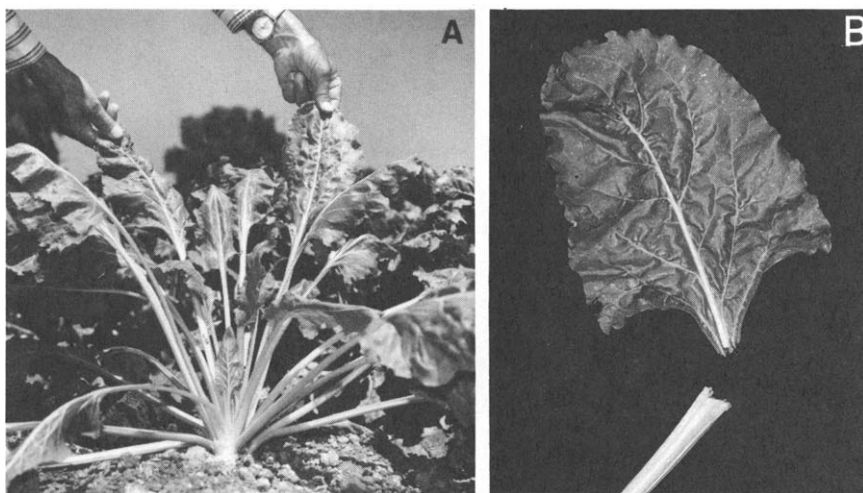


Fig. 16-3. Select a recently matured leaf, one that has just reached full size. There are four or five such leaves, similar to the two being held (A) on each plant. Separate blade from petiole where they join (B).

Dry material is preferable to fresh as concentrations tend to be less variable, laboratory work can be more routinely scheduled, and material can be easily stored for additional analyses in the future. The chief disadvantage of reporting results on a dry weight basis occurs through the dilution of nutrients by increasing dry matter accumulation in plant tissues as they mature. This diluting action, however, may be minimized at each sampling date by the selection of plant material of the same physiological age. For this reason, plant material from the youngest "mature" leaves (youngest fully developed leaves) is selected for analysis whenever possible.

The establishment of critical concentration values of NO_3^- -N and H_2PO_4^- -P in petioles, K in blades and petioles, and for SO_4^{2-} -S and Zn in blades of recently matured sugarbeet leaves is illustrated in Fig. 16-4, 16-5, 16-6, 16-7, and 16-8. Similarly, critical concentrations have been determined for other nutrients as indicated in Table 16-1.

B. Interpretation

When monitoring plants in the field, the likelihood of a growth response from the addition of fertilizer will depend upon whether the nutrient concentration of the plants sampled is above or below the critical level. When the nutrient concentration is above the critical level and remains there throughout the entire growth period, there is little chance of a response in growth from the addition of more nutrient. Conversely, when the nutrient concentration falls below the critical level the chance of a growth response under field conditions becomes much greater as the nutrient concentration in the plants decreases. The magnitude of the response will depend on the relative adequacy of other growth factors, upon the stage of growth when

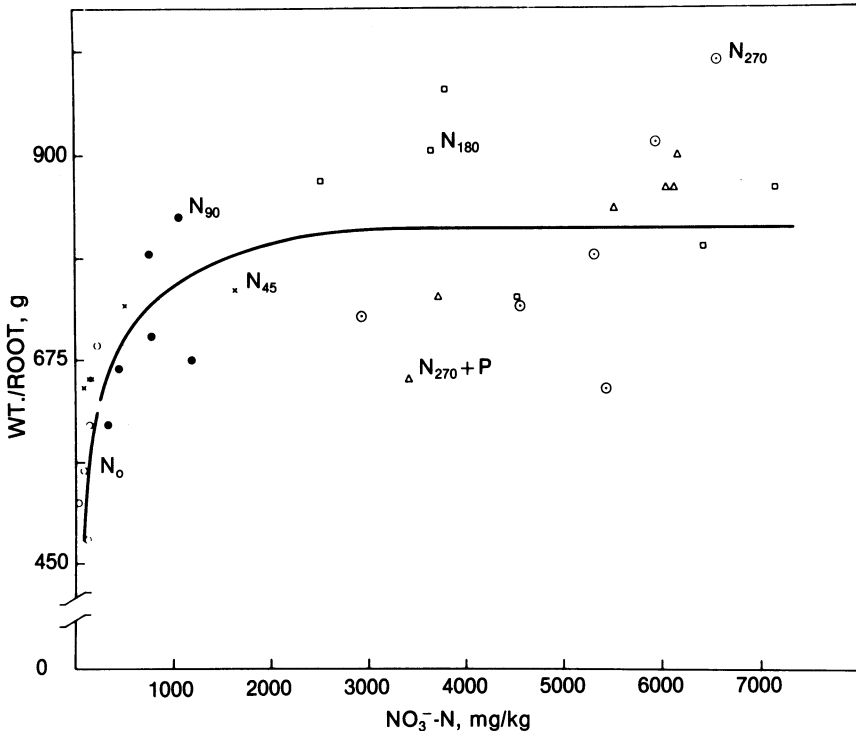


Fig. 16-4. Relation of beet-root fresh weight to the $\text{NO}_3\text{-N}$ concentration (dry basis) of petioles of recently matured leaves from a field experiment near Woodland, CA. Subscripts indicate kilograms of applied N/ha and P indicates 97 kg of applied P/ha. The critical N concentration at the breaking point of the curve is about 1000 mg of $\text{NO}_3\text{-N}$ /kg. Below the critical concentration growth is retarded, but above it growth is maintained at maximum as long as there are no other factors limiting growth (Ulrich, 1950).

the deficiency occurs and the length of time it persists. When other growth factors are sufficient, addition of the deficient nutrient will result in a relatively large increase in yield. When another factor or set of factors becomes limiting almost immediately, additions of the required nutrient will produce a relatively small increase in yield. Similarly, the chance of a measurable growth response in the field will decrease as the duration of the deficiency decreases. If the deficiency first appears late in the growth season, there is little chance for a significant yield increase.

When a sample consists of plant material taken from a large area within a field, the leaves taken may differ considerably in nutrient concentration. Consequently, when the average concentration of the sample is at or near the critical level, the material collected will represent both deficient and non-deficient plants. Under these conditions, yields will be raised significantly by fertilization only when the proportion of deficient to nondeficient plants is sufficiently large to produce a measurable increase in yield. Thus, the critical level associated with a significant yield increase will be higher under most

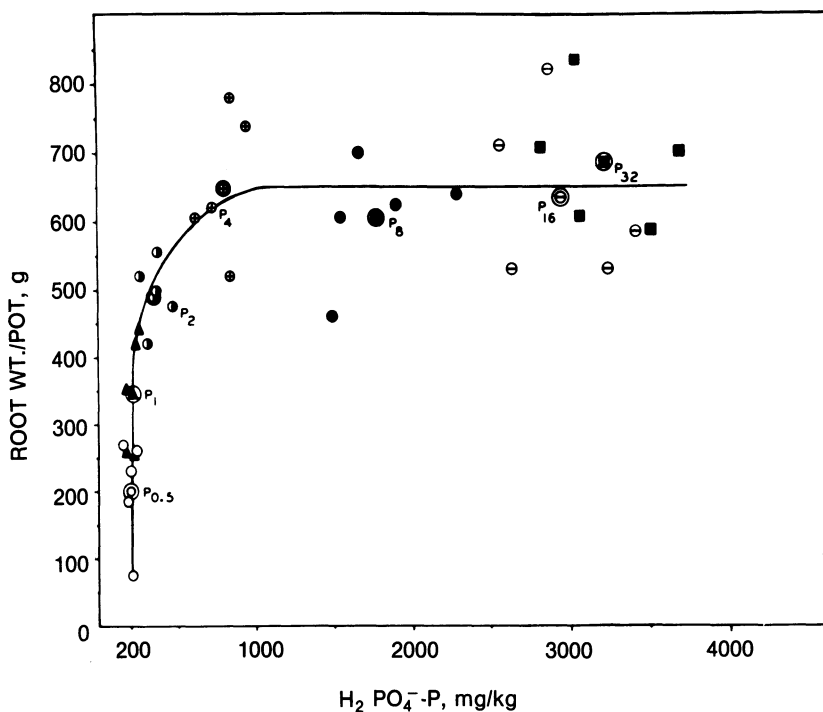


Fig. 16-5. Relation of beet-root fresh wt. to $\text{H}_2\text{PO}_4\text{-P}$ conc. (dry basis) in petioles of recently matured leaves in a pot experiment. The critical conc. is approximately 750 mg/kg. The subscripts are increments of 434 mg of P/pot (49 kg/ha), e.g., $P_2 = (434)2 = 868$ mg of P/pot, the circled points are average values for a treatment level.

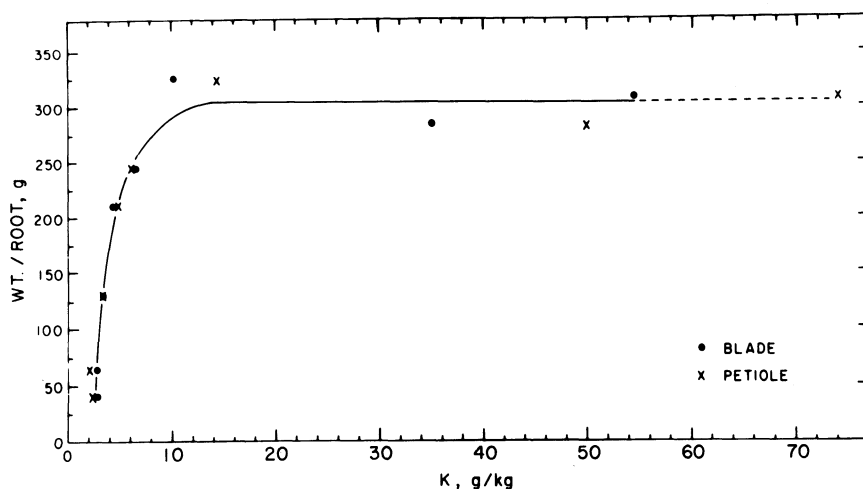


Fig. 16-6. Relation of beet-root fresh wt. to K conc. in petioles and blades (dry basis) of recently matured leaves of plants in culture solution receiving increasing amounts of K and a constant but adequate amount of Na. The critical K value is approximately 10 g/kg (1.0%) for blades, regardless of Na content, and for petioles only when Na conc. is > 15 g/kg (1.5%). Each symbol is an average of five replications.

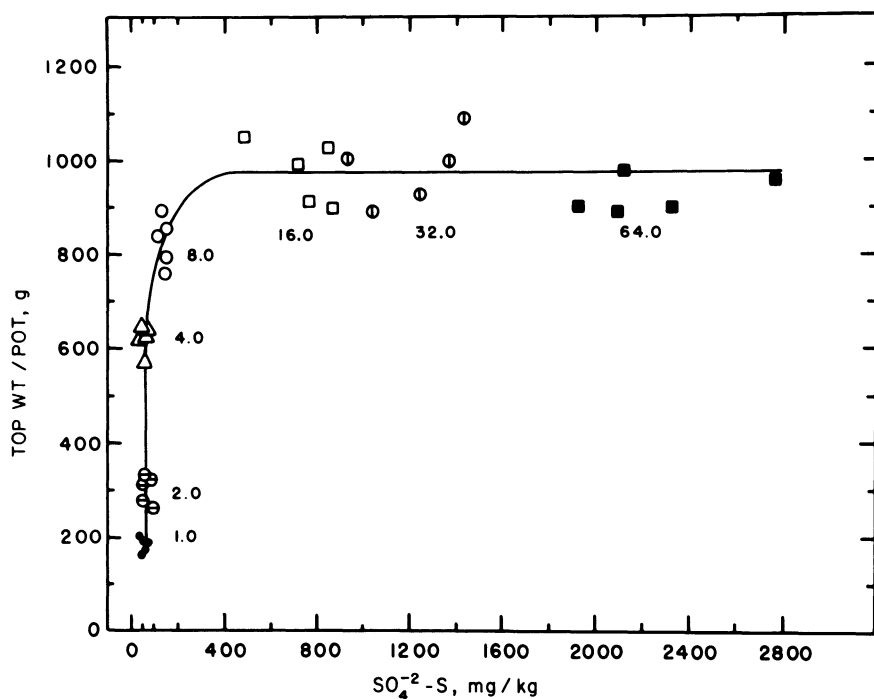


Fig. 16-7. Relation of fresh wt. tops to $\text{SO}_4^{2-}\text{-S}$ conc. (dry basis) of recently matured blades of plants in culture solution. Numbers adjacent to symbols are $\text{mg SO}_4^{2-}\text{-S/L}$ initially in the culture solution. The critical conc. at the breaking point of the curve is approximately 250 mg/kg .

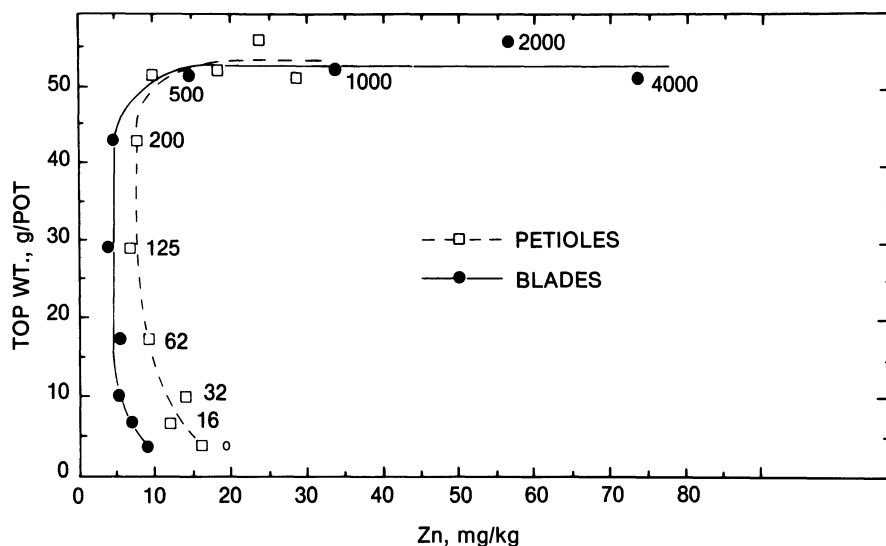


Fig. 16-8. Relation of dry wt. of tops to Zn conc. (dry basis) of blades and petioles of recently matured leaves (Rosell & Ulrich, 1964). Each symbol is the mean of five replications and the numbers adjacent are micrograms Zn as $\text{ZnSO}_4/20\text{ L}$ of initial culture solution. Blades are preferred for analysis because of the broad range in conc. from deficient to adequate. The critical value for blades is approximately 10 mg/kg .

field conditions than when samples are taken from solution or pot cultures, or from small, uniform field plots.

C. A Constant or Changing Critical Value?

Nutrient concentrations in leaves that are increasing in age tend to reflect the characteristics of leaves of that particular age, whereas properly sampled leaves of the same physiological age tend to reflect the changing nutrient status of the plants as influenced by the balance between nutrients supplied from the soil and nutrients required for plant growth. For sugarbeet, where vegetative growth is indeterminate, if the leaf sampled is always of the same physiological age, critical concentrations have not been found to vary enough, regardless of the stage of growth of the plant, to affect their usefulness as a measure of the nutritional status of the plants at the time of sampling (Ulrich, 1964). We have found the concept of the constant critical concentration for several nutrients to be a satisfactory reference point for evaluating the nutrient status of plants throughout the varied growing seasons in California (Ririe et al., 1954), for other states (Robins et al., 1956; Carter et al., 1971), and for other countries (F.J. Hills, 1965–1985, unpublished data).

An exception to the constant critical value is for the evaluation of the nutrient status of seedling plants before a large mature true leaf has developed. In this case, it is advisable to determine the critical concentration for various nutrients for a specific seedling plant part as was done by Sipitanos and Ulrich (1969) for H_2PO_4^- -P in various parts of sugarbeet seedlings (Table 16-1).

D. Effect of Other Factors

Variety (cultivar) of sugarbeet apparently has little or no effect on the critical concentration. So far, we have not observed a significant difference in the critical concentration among commercial varieties. Effects of variety on the critical level, if any, are expected to be small compared to the wide range in nutrient concentrations between plants with and without an adequate supply of a given nutrient.

Concern is frequently expressed that the moisture regime under which plants are growing may have serious effects on nutrient concentrations and critical concentrations. Loomis and Worker (1963) found that moisture stress had little effect on the concentration of NO_3^- -N in mature petioles compared to plants recently irrigated and not exhibiting moisture stress systems. We have observed the same effect (Table 16-2). Even when plants were severely stressed, i.e., wilted to the point where many old leaves were lost, there was little or no reduction in the NO_3^- -N concentration in mature petioles. Thus, it appears that moderate changes in weather or the time of day that samples are collected will have little influence on nutrient concentration, particularly from the standpoint of making decisions as to whether plants are deficient in a certain nutrient.

Table 16-2. Effect of moisture stress on the concentration of NO_3^- -N in petioles of recently matured sugarbeet leaves, Kern County, California (F.J. Hills, 1963, unpublished data).

Days from last irrigation	Observed plant stress to soil moisture	NO_3^- -N, mg/kg (dry basis)
<u>22 July</u>		
2†	None	3030
20‡	Moderate	3270
		SE = 590
<u>31 July</u>		
11†	Slight	4370
29‡	Severe	4330
		SE = 850

† Sixteen plots last irrigated 20 July.

‡ Sixteen plots last irrigated 2 July.

Nutrient concentration, however, can be markedly changed by other conditions that affect plant growth. For example, petioles of mature leaves of sugarbeet infected with the beet yellows virus may be higher in NO_3^- -N concentration than healthy plants (Table 16-3). This difference is not indicative of a different nutrient requirement in the diseased plants, but is the result of NO_3^- -N accumulation in the slow-growing plants.

When there are differences in nutrient concentration associated with variety, weather, moisture stress, and disease they are likely to be related to the kind and extent of root development, or to other factors affecting growth, rather than to differences in internal requirements (Ulrich, 1948a, b).

Table 16-3. The effect of variety and virus infection on the concentration of NO_3^- -N in petioles of recently matured sugarbeet leaves, Broom's Barn Exp. Stn., England (F.J. Hills, 1970, unpublished data).

Variety	NO ₃ ⁻ -N, mg/kg (dry basis)		Variety means
	Healthy	Diseased†	
27 July (V × D = NS)			
US H7A	2880	6410	4650
US H9B	3120	4680	3900
Bush Mono	3660	5240	4450
Disease means	3220	5440**	NS‡
24 Aug. (V × D = NS)			
US H7A	3060	4460	3760
US H9B	3570	4640	4120
Bush Mono	2970	4590	3780
Disease means	3210	4560**	NS

** Significantly greater than healthy ($P < 0.01$).

† Inoculated with the beet yellows virus on 8 June, soon after thinning.

‡ NS = Not significant.

II. USE OF PLANT ANALYSIS

Experience in the interpretation of nutrient concentrations in plant samples, as related to critical levels, is essential for giving advice concerning fertilizer practice. Optimum economic yield is the usual objective, but fertilizing sugarbeet for maximum top and root production usually does not mean maximum sucrose production. An adequate supply of N is required early in the growing season to ensure vigorous top and root growth, but if storage roots are to be high in sucrose concentration, the plants must be N deficient for a period prior to harvest to retard vigorous growth, especially top growth, and allow sucrose to accumulate in the storage roots. The field experiment summarized in Fig. 16-9 illustrates this. Optimum sugar yield, a function of root yield and sucrose concentration, was produced at a fertilizer rate that nearly optimized root yield, but this rate was considerably less than the rate required for maximum crop growth (roots plus tops) and was not the rate giving the highest root sucrose concentration (Hills et al., 1978).

Fertilizing to just achieve optimum sugar yield has other advantages. It seldom contributes to NO_3^- pollution of groundwater and, in addition, a considerable amount of N is incorporated into beet tops where, like a green manure crop, a portion is available to the next crop to be grown on the field (Hills et al., 1978; Abshahi et al., 1984). Table 16-4 gives data from the same experiment as Fig. 16-9 and shows that 223 kg of N/ha was removed in the

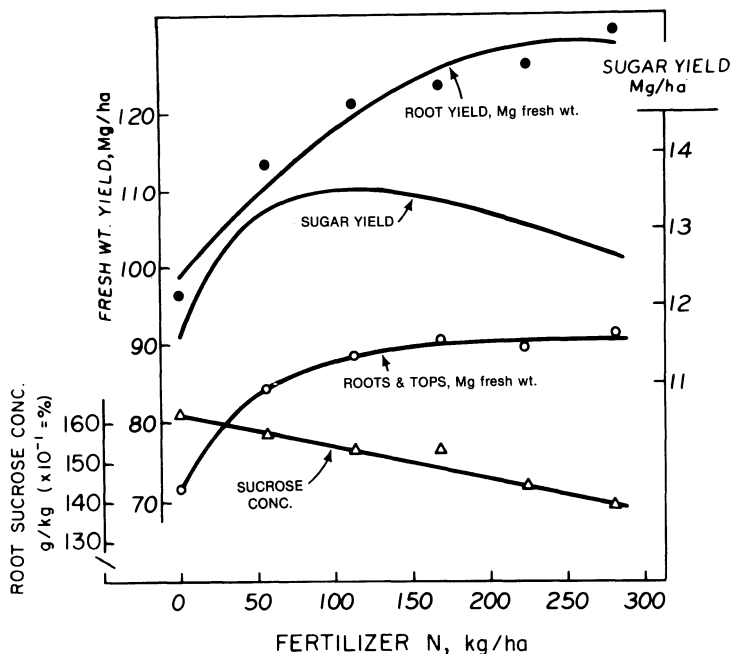


Fig. 16-9. Response of sugarbeet to fertilizer N (Hills et al., 1978). The response functions are: root + tops, $Y = 98.66 + 0.24X - 0.00047X^2$, $R^2 = 0.96$; root yield, $Y = 90.88 - 19.21(0.981^X)$, $R^2 = 0.99$, % sucrose, $Y = 16.2 - 0.0079X$, $r^2 = 0.95$. Sugar yield is computed from root yield and sucrose concentration.

Table 16-4. Response of sugarbeet to fertilizer N and resulting N uptake. (Values are predicted from regressions [Hills et al., 1978].)

Fertilizer N applied	Sugar yield	Fresh wt. yield			N uptake		
		Tops	Roots	Total	Tops	Roots	Total
kg/ha		Mg/ha			kg/hg		
0	11.6	27.0	71.7	98.7	79	79	158
56	13.3	29.3	84.3	113.6	93	101	194
112	13.6	42.8	88.6	131.4	105	118	223
168	13.4	62.1	90.1	152.2	114	132	246
224	13.1	85.4	90.6	176.0	112	141	263
280	12.7	111.9	90.8	202.7	127	147	274

crop that required 112 kg of fertilizer N/ha to give optimum sugar yield. Of the 223 kg of N/ha taken up, only 47% came from the applied fertilizer. Thus, when carefully fertilized, a sugarbeet crop may be viewed as a scavenger crop in terms of its extensive use of soil N (Hills et al., 1983). Figure 16-10 shows the time course of the concentration of NO_3^- -N in sugarbeet petioles for certain N rates of the experiment of Fig. 16-9 and Table 16-4. The petioles of sugarbeet fertilized for optimum sugar yield indicated a N deficiency (< 1000 mg of NO_3^- -N/kg) for about 8 wk prior to a fall harvest. This, and much additional experience, indicates that plants should be deficient for at least 4 wk and as long as 10 wk before harvest.

The predictability of a response to fertilizer added in response to a low concentration of a nutrient in plant tissue decreases as the time elapsed from

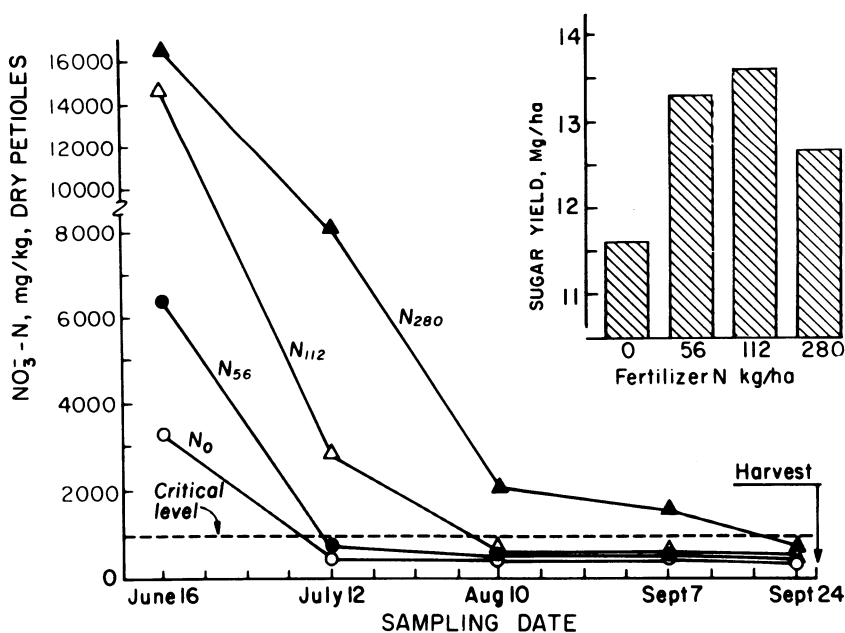


Fig. 16-10. Petiole nitrate depletion curves for selected fertilizer N rates and related sugar yields of the experiment of Fig. 16-9. For the optimum rate of N fertilization (112 kg of N/ha) plants were N deficient for about 8 wk prior to harvest.

sampling to harvest increases. This is because climate and other factors intervening between sampling and harvest may greatly alter soil nutrient supply or plant nutrient demands. For best results in developing a plant analysis program, sampling should be done frequently to establish the proper time and frequency of sampling. This approach is much preferred to depending on the results of a single sampling, as is too often done. A single mid-season sample will not detect an early P deficiency that disappears as soil temperatures warm or a post mid-season release of N mineralized from the organic residue of a previous crop.

Following are ways in which plant analysis can be used to improve crop production.

A. Evaluation of Fertilizer Programs

To determine how well a fertilizer program is meeting the needs of a sugarbeet crop, a series of samples must be taken throughout the growing season. One set of samples should be taken early to detect early season deficiencies of certain nutrients, particularly P (Hills et al., 1970). Subsequent samplings should be at 2- to 4-wk intervals (Fig. 16-10 and 16-11). The minimum number of samplings should be four: one at thinning time, one at early mid-season, one at late mid-season, and one just prior to harvest. By comparing the analyses of these samples to critical nutrient concentrations, it is possible to determine how well the fertilizer program is meeting the needs of the crop. In this manner, impending nutrient deficiencies can be detected

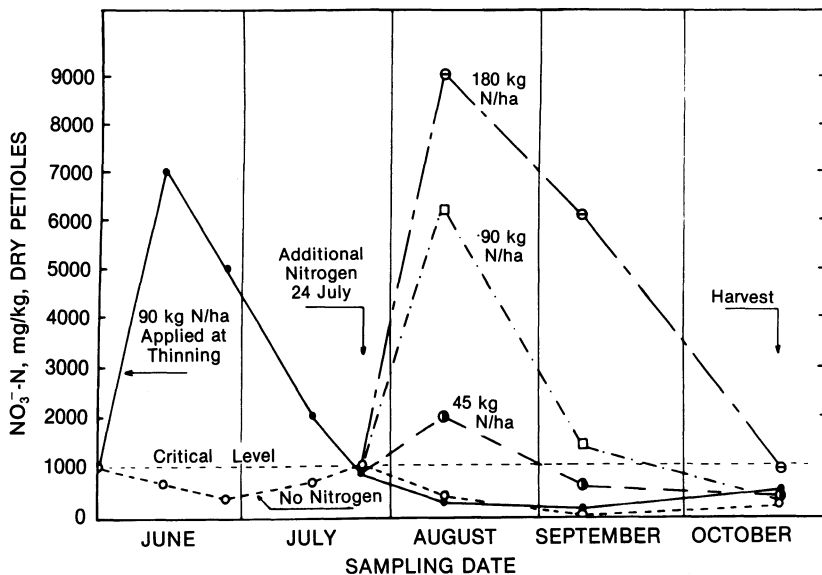


Fig. 16-11. Controlled feeding. The study showed that 90 kg N/ha at thinning was not enough. A second 90 kg of N/ha in mid-July gave the highest sugar yield. Sugar yields (Mg/ha) at harvest for the various N rates (kg/ha) were: Zero N, 7.5; 90 N, 8.2; 90 N + 45 N, 8.8; 90 N + 90 N, 9.4; 90 + 180 N, 9.2 (Ulrich et al., 1959).

and corrected before they occur and appropriate adjustments in a fertilizer program can be made. This system, particularly if it can be applied to more than the sugarbeet crop in a rotation, offers an excellent way to optimize fertilization efficiency. If an impending deficiency is discovered early enough in the growing season, emergency applications of fertilizers may be made to correct the deficiency. However, with more experience and consistent use of plant analysis, emergency applications of fertilizers will become a rarity or completely unnecessary. Adjustments in the fertilizer program often will be limited to increasing the use of one nutrient or lessening that of another, or even adding other elements just becoming short in supply. Also, changes in timing or method of fertilization might be necessary to satisfy more fully the fertilizer needs of the crop.

After alterations in fertilization or cultural practices have been made, the nutrient changes occurring within the crop should again be observed through plant analysis. If the new program leads to better nutrition of the crop and higher sugar yields, it is continued; if not, the program is changed again, thus preventing deficiencies and serious losses in crop yield.

B. Controlled Feeding

Fertilizing crops with N on a demand basis is desirable from the standpoint of maximizing net returns and minimizing potential contamination of groundwater. This can be accomplished for the sugarbeet crop by applying a minimum rate of fertilizer N initially, then waiting until results of plant analysis show a need for more N (Hills et al., 1982). Nitrogen-deficient plants often produce more sucrose than N-sufficient plants unless deficiencies occur more than 10 wk prior to harvest. With longer periods of deficiency, more sucrose is produced by N-sufficient plants due to their more rapid root growth. Thus, an objective of N fertilizer management should be to allow plants to become N deficient prior to harvest. If an error is to be made it appears desirable to make it on the side of underfertilization, since periods of deficiency of up to 10 wk usually can be tolerated without reducing sugar yield (Hills et al., 1963).

The adequacy of an initial fertilizer application can be ascertained from petiole analyses by taking samples from recently matured leaves at 2-wk intervals starting about 2 wk after thinning (Fig. 16-11). Indications of impending deficiencies of more than 10 wk prior to harvest can be estimated based on local experience, or as calculated by Carter et al. (1971) or Hills et al. (1982). Such deficiencies can be corrected by additions of from 45 to 65 kg of N/ha.

C. Diagnosis of Abnormal Growth

Frequently, plants in all or part of a field show abnormal growth characteristics. A knowledge of nutrient deficiency symptoms may lead to a tentative diagnosis, which can be confirmed or discarded by analyses of comparable petioles and blades from abnormal and normal appearing plants (Ulrich &

Table 16-5. Leaf analyses of vigorous and poorly growing sugarbeet reveal S deficiency (Ulrich et al., 1959).

Growth of sugarbeets	Leaf analysis, dry basis			
	Petioles			Blades
	$\text{NO}_3^- \text{-N}$	$\text{H}_2\text{PO}_4^- \text{-P}$	K	$\text{SO}_4^{2-} \text{-S}$
	mg/kg		g/kg	mg/kg
Vigorous	2520	2120	31.5	1880
Poor	9000	2990	38.0	155

Hills, 1969). Plants should be sampled soon after deficiency symptoms appear. After a prolonged period of deficiency, the concentration of certain nutrients will increase in physiologically mature tissue even though the symptoms remain. Table 16-5 illustrates how plant analysis was used to detect a S deficiency in sugarbeet. A large area in a field contained plants that appeared deficient. However, analyses indicated that N, P, and K were all above their critical levels but that $\text{SO}_4^{2-} \text{-S}$ in blade tissue was deficient. Fertilizer treatments applied to the plants in the affected area confirmed the diagnosis.

The critical nutrient concentrations and nutrient concentrations associated with deficiency symptoms given in Table 16-1 are helpful in diagnosing abnormal plant growth.

D. Guide to Harvest

When there is a choice of fields to be harvested, the results of a systematic plant analysis program may serve as a guide to the scheduling of beet harvest (Duckworth & Hills, 1952). Those fields with the longest period of N deficiency would be scheduled for an early harvest and those high in this nutrient would be delayed until depleted or held as long as possible before harvesting.

Root pulp being analyzed for sucrose can be analyzed for NO_3^- through the use of the NO_3^- electrode or semiquantitatively through the use of the diphenylamine reagent. These tests were first implemented by John T. Alexander (Holly Sugar Company) following a field demonstration by Albert Ulrich as to the use of the diphenylamine reagent to locate NO_3^- in roots and leaves of sugarbeet. They have been useful in revealing areas of low sucrose concentration due to excessive nitrate uptake prior to harvest (Hills & Ulrich, 1971). Sugar companies have found these tests useful in evaluating how well crops in an area have been fertilized with N to meet desirable quality standards. When pulp $\text{NO}_3^- \text{-N}$ values at harvest are coupled with petiole $\text{NO}_3^- \text{-N}$ values for the entire growing season, the grower learns when and for how long the beets were high or low in $\text{NO}_3^- \text{-N}$ before harvest. This information will help in meeting the quality standards required for processing beets efficiently.

E. Nutrient Survey

Plant analysis can be used to survey the nutrient status of crops in a farming area (Duckworth & Hills, 1952). This can result in the detection of deficiencies, improvement of fertilizer practices, and the identification of fields suitable for fertilizer trials. To be fully effective, the plant nutrient survey should include a series of samplings during the growing season, as outlined earlier under the evaluation of fertilizer programs.

III. SAMPLING PROCEDURE

To serve as a measure of variability within a field, a minimum of two samples, but preferably four, should be taken from each field. The number of leaves for each sample depends on the variability between leaves but usually from 25 to 50 leaves are sufficient to estimate reasonably the true mean of the nutrient concentration in the plants represented by the sample (Ulrich & Hills, 1952).

One system to follow in sampling a field is to divide it into imaginary quarters (Hills et al., 1982). The sampler walks across the center of each quarter at right angles to the plant rows and collects from 25 to 50 leaves per quarter of the field. Samples should be placed in an ordinary paper bag of convenient size and taken to the laboratory for processing as soon as possible. Delays of more than 48 h at ordinary temperatures should be avoided, and storage in closed compartments of automobiles during warm weather should not be allowed. If it is necessary to store samples prior to drying, they should be kept at a temperature of 5 °C. At this temperature, concentrations of NO_3^- -N, H_2PO_4^- -P, and K on an air-dry basis change very little in sugarbeet petioles over a 120-h period (Ulrich, 1948a).

For micronutrient analyses, plant material must be free of dust. Leaves should be washed for 30 s in a bath containing a detergent or a detergent and 0.1 M HCl, followed by two successive rinses in distilled water.

A sample may be reduced in size by cutting it into small pieces (about 10 mm) thoroughly mixing the pieces, and placing a subsample (about 100 g of fresh material) in a cut-down paper bag or other suitable container and drying it overnight in an oven, preferably with a forced draft at 70 °C. After drying, the samples are ground to pass a 30- or 40-mesh screen and stored in small glass or plastic vials. Following this procedure, samples have been kept in moisture-tight containers for many years without a significant change in their mineral composition.

IV. ANALYTICAL METHODS

The methods selected for analyzing plant material must be both accurate and rapid. There is little merit in analyzing a few samples accurately during the course of a day, when there are hundreds of samples to be analyzed, nor

is there much value in analyzing hundreds of samples rapidly when the analytical error is equal to or greater than the sampling error of the material analyzed. Whenever feasible, the analytical error should be far less than the error associated with the plant material sampled (Ulrich & Hills, 1952).

The time lapse between collection of samples and reporting of results must be as brief as possible if a current season crop is to benefit. Information for efficient fertilizer practices can be provided conveniently within 3 to 7 d by the laboratory methods proposed by Johnson and Ulrich (1959) or by more recent methods involving atomic absorption spectroscopy, atomic fluorescence spectroscopy, inductively coupled plasma (ICP) emission spectrophotometry, and the specific ion electrode. As a check on the analyst and the analytical method, it is important to carry along with the unknowns a reference plant sample of known nutrient concentration established by many analyses.

V. LIMITATIONS AND USEFULNESS

The concentration of a mineral nutrient in the tissue of a specified plant part, when referred to a well-established critical concentration, provides a simple way of determining whether the plants represented by the sample are adequately supplied with nutrients at the time of sampling. Such analyses, however, usually reveal only one deficiency at a time. A second nutrient, or even a third nutrient, may be in short supply but, due to reduced growth caused by the primary deficiency, most other nutrients will accumulate in the tissue. When the primary deficiency has been corrected, the increased growth will often decrease the concentration of a second, nutrient which most likely will become deficient rather soon. Conversely, in the case of a P deficiency, NO_3^- uptake has been observed to be depressed, and the depression reversed by the addition of P to the soil or a nutrient solution that lacked P (Sipitanos & Ulrich, 1969; Hills et al., 1970).

A nutrient level below the critical concentration at a single sampling date indicates a deficiency, but later the same plants may show an increase in nutrient uptake. For this reason, multiple sampling dates are preferable to a single sampling date. In the interpretation of the results for multiple sampling dates, the sharper the drop in nutrient concentration and the earlier in the season it occurs, the greater the degree of deficiency. But even when the results of several sampling dates indicate that plants have been deficient for a considerable period, the exact degree of deficiency is not known (Hills et al., 1963). At harvest, however, the degree of deficiency for a given field can be estimated in terms of the maximum yield for the area, and fertilization of the next crop is then adjusted to this finding. For example, a field that produced only 25% of the potential yield, with all other growth factors adequate, is much more deficient and will require more fertilizer than one that produced 90% of the potential for the area.

One of the greatest values of plant analysis is the prevention of deficiencies rather than their correction after they occur. Trends in leaf concen-

tration followed over a period of years can be a valuable guide in delineating the kinds, amounts, frequency, and methods of fertilization for efficient crop production on a given field. In this way, a nutrient deficiency can be predicted or at least detected as soon as it occurs, and corrective measures can be taken before serious crop losses take place.

Plant analysis is often useful in revealing the subtle influence of climate on the supply and demand for nutrients. In a favorable climate, the need for nutrients, particularly for N, increases dramatically during the grand growth period and then declines prior to harvest. During periods of rapid growth, soil N supplies may not be adequate to meet the needs of the crop, but later as the growth rate declines, soil NO_3^- -N may exceed demand just when it should be deficient prior to harvest. Such excesses can occur from nitrification of organic material in peat soils, previous crop residues, or heavy applications of manure. However, low night temperature shortly before harvest, will frequently increase sucrose concentrations even in the presence of high petiole NO_3^- -N values.

Plant analysis results have also revealed that low soil temperatures induce P deficiency of seedlings on some soils relatively high in P. This deficiency is overcome by P fertilization prior to planting and later by an increase in soil temperature.

Growth rates and the need for nutrients are also greatly influenced by day length, day and night temperature, light intensity, and rainfall, which may move NO_3^- in surface soil into the root zone and thereby lower sucrose concentrations of beets as new growth occurs (Stout, 1964). Comparing plant analysis results, soil N values, and root pulp NO_3^- -N tests with sugar produced on each field within and among districts will be useful to the grower, processor, and agronomist in assessing growth problems and fertilizer practices.

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Chapter 17

Plant Tissue Analysis of Sugarcane

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Sugarcane (*Saccharum officinarum* L.) is a highly efficient plant photosynthetically, producing up to 40 t of sugar/ha in Hawaii where it is normally grown as a 24-mo crop (Clements, 1964a, 1980; Clements et al., 1952). These excellent yields result from optimization of the myriad factors that affect the crop's growth and development.

The grower cannot control such parameters as minimum and maximum daily temperatures, and intensity and duration of sunlight, of course. He only has partial control of soil moisture if the field is not irrigated.

A grower does have significant control over another important parameter, however; i.e., crop nutrition and availability of essential nutrients in the soil. His obvious goal is to maintain soil fertility at a level that allows maximum potential crop productivity.

Excessive nutrient availability, on the other hand, can be detrimental to profitable yields in any of three ways: (i) some essential nutrients; e.g., B and Mn, are toxic to sugarcane when too much is available, (ii) excesses of some nutrients; e.g., N, interfere with the "ripening" of sugarcane and thus decrease sugar yields; and (iii) overfertilization, a common cause of excessive availability, erodes profits.

It is sometimes a fine line indeed between adequate and excessive availability of a nutrient, especially a micronutrient. As you might anticipate, much research has been done to develop techniques and procedures to assist sugarcane growers in coping with this problem. The most accurate and successful ones to date are those based upon analysis of the plant tissues to assess the crop's nutritional status. Further improvement in usefulness is gained when environmental factors that affect nutrient uptake, accumulation, and utilization are integrated into the tissue analysis program.

I. HISTORY

The concept of analyzing plant tissues to evaluate a crop's nutritional status and determine its future fertilizer requirements is certainly not new,

dating instead from the mid-19th century work of Liebig (Samuels, 1969). It was not until the 1930s, however, that Lagatu and Maume provided the scientific basis for what today we know as "foliar diagnosis" or "plant tissue analysis" (Lagatu & Maume, 1932, 1933a, b). The idea is that certain tissues of a growing plant can be chemically analyzed to measure their essential nutrient contents and, therefore, to measure indirectly the supply of nutrients available in the soil. As we now realize, the assumption that the plant nutrient content is a direct function of nutrient availability in the soil is not always true. When the availability of a nutrient is inadequate, its concentration in the plant tissues drops below a previously defined optimum amount or "critical level." The latter represents a marginal insufficiency that causes a slight reduction in growth without producing visible deficiency symptoms or decreasing crop yield.

II. REVIEW OF TISSUE ANALYSIS METHODS USED FOR SUGARCANE

A. Methods Based on "Critical Level" Concept

In 1936, Halais (1950, 1955, 1957) began experimenting in Mauritius with a foliar diagnostic technique for sugarcane patterned after methods developed for other crops by Lagatu and Maume (1932, 1933a, b). Halais correlated tissue analysis data for N, P, and K with field responses to fertilizers. This led to establishment of critical levels for these nutrients. Nitrogen, P, and K fertilizer recommendations could then be made by comparing the tissue concentrations of these nutrients to the critical levels. The Halais method became known as the top visible dewlap (TVD) sampling procedure and is still used in some regions today, especially those where sugarcane is grown as a 11- or 12-mo crop (Samuels, 1969). The TVD leaf is the youngest leaf with a visible dewlap, often the third leaf from the spindle.

The TVD samples are typically taken 4 to 6 mo after the cane is ratooned; the plant crop is not usually sampled with this diagnostic method. This timing usually corresponds to the peak of the "grand growth period" or "boom stage." Two samples are taken during the 12-mo crop cycle with a minimum interval of 1 mo between them. A sample consists of TVD leaves removed from 50 to 60 plants along a diagonal through the field.

These leaves are weighed, and then four discs are punched from each blade, halfway between the midrib and the margin. Alternatively, the entire middle one-third of the blade, excluding the midrib, may be used. The selected tissue is then dried, ground, and analyzed for its mineral nutrient content.

B. Crop Logging

Clements started studying the effects of climate on sugarcane growth and yield in Hawaii in 1940 (Clements, 1940, 1980). He quickly showed that the effects of climatic, physiological, and nutritional factors on a 24-mo sugar-

cane crop were closely inter-related. Clements' tissue analysis methods were later adopted by the Hawaiian sugar industry and are now called *crop logging*. Crop logging has undergone frequent revision and extensive improvement in the succeeding decades but its scientific basis remains unchanged (Clements, 1940, 1959, 1964b, 1980; Sund & Clements, 1974). This foliar diagnostic method is often acknowledged as the most comprehensive method used today for evaluating and guiding the growth and development of sugarcane (Samuels, 1959, 1969; Jones & Bowen, 1981).

Plant tissue samples are taken every 35 d throughout the 24-mo crop cycle. However, crop logging has also been adapted to the more common 12-mo crop. In the latter case, the cane is sampled at 14-d intervals rather than the originally suggested 35-d ones (Sund & Clements, 1974; Clements, 1980).

Regardless of the frequency of sampling, though, the elongating sheaths of leaves 3, 4, 5, and 6 (spindle leaf = 1) are removed from the primary stalks of five plants. It is very important that primary stalks *only* be selected because physiological age of the tissue affects nutrient composition. These sheaths are used for fresh weight and tissue moisture content determinations, for total sugar content analysis, and for all other nutrient analyses except N. The latter is measured in leaf punches taken from the blades of these same leaves. (For a discussion of the leaf-numbering system used in crop logging, see Clements & Ghotb, 1969.)

Numerous other data are obtained from the three samples taken during the midpoint or "boom stage" of the crop cycle, usually when the cane is 8- to 12-mo old. The three "boom stage" samples are analyzed for phosphate and the micronutrients. (Micronutrients as used here includes all essential nutrients other than N, P, and K, a convention adopted from the Hawaiian sugar industry.)

Six to 10 crop log samples are taken during an 11- to 12-mo crop, and about 22 samples during a 24-mo crop.

Crop logging differs from many other foliar diagnostic procedures in that it integrates essential nutrient contents of sugarcane tissues with plant growth, sugar production, and various climatic factors known to affect these parameters (Clements, 1940, 1959, 1964a, 1980). The crop logging system was developed in Hawaii under conditions that differ significantly from other regions of the world where sugarcane is grown. Primarily, this is 24-mo crop in Hawaii, irrigated in some areas and subjected to as much as 250 cm of rainfall annually in others, and grown from sea level to 600 m elevation. However, crop logging has been modified locally for use under each of these diverse conditions. This system for monitoring crop development has also been adapted for application in areas beyond Hawaii (e.g., regions of Iran, Iraq, Brazil, and Ecuador).

Researchers at the Hawaiian Sugar Planters' Association (HSPA) were also working on sugarcane tissue analysis, but not foliar analysis, during this period (Samuels, 1959, 1969). The stalk-logging technique, devised by Burr, dictates that 8 to 10 internode samples be taken monthly, starting when the 24-mo crop cane is 6- to 10-mo old and continuing until the last fertilizer

has been applied. The stalk is cut below the point of attachment of leaf 10, retaining any older leaves that may be present. Five such stalks constitute a sample. The stalks are then trimmed so that only internodes 8, 9, and 10 remain. These are sliced, dried, ground, and analyzed for N, P, and K (Burr, 1955).

Ewart, also working at the HSPA, developed the self-adjusting stalk indices method. This technique, like that of Burr (1955), was predicated upon the hypothesis that the stalk would be a more reliable indicator of the nutritional status of the plant than would the leaf blades and sheaths. A sample consists of all stalks from pre-selected small, medium, and large sugarcane stools that have been preferentially fertilized. Similar samples are taken from the adjacent commercial field. The stalk tissues are analyzed for N, P, K, and Ca (Samuels, 1959, 1969). Neither this method (Samuels, 1959, 1969) nor that devised by Burr (1955) has gained much acceptance among the world's sugarcane growers, however.

The TVD method developed by Halais (1950, 1955, 1957) was subsequently modified by Evans to include adjustments for crop age at sampling and the amount of rainfall prior to sampling (Evans, 1955). Evans also established TVD critical levels for some of the micronutrients (Evans, 1955).

Numerous other techniques, many of which are regional modifications and adaptations of these methods, are also in use; e.g., the Jamaican and Puerto Rican versions of the TVD method (Samuels, 1959, 1969).

The Jamaican method, as developed by Innes and Chinloy (1955), requires sampling of the blade of the third fully-expanded leaf when the crop is 4- to 5-mo old. The crop field is sampled as is a microplot previously established within the crop field. These tissues are analyzed for N, P, and K. The microplot has received more N fertilizer than the surrounding field. Leaf N concentrations in the crop cane are compared to those from the microplot cane. Nitrogen fertilizer recommendations are made, based upon relative increases in N contents. Potassium and P needs are determined by comparing current data to those from earlier crops.

The Puerto Rican method is similar to crop logging in that leaves 4, 5, and 6 are sampled (Samuels, 1959, 1969). However, the blades and sheaths are combined for N, P, and K analyses, whereas tissue moisture content is determined in the sheaths alone. Samples are usually taken only in cane that is 3-mo old or less. If older cane is sampled, then corrections are made for crop age and tissue moisture content. Fertilizer recommendations are then made, based upon previously determined standard values.

The methods developed in Jamaica (Innes & Chinloy, 1955), Mauritius (Halais, 1950, 1955, 1957), and Puerto Rico (Samuels, 1959, 1969) are particularly well suited to sugarcane when it is grown as a 12-mo crop but have little applicability to longer crop cycles. The provision for early sampling allows corrective fertilizer applications to be made to the current crop. However, no corrections are made for crop age and tissue moisture content in the early samples despite the fact that these parameters are known to have significant effects upon uptake and accumulation of N and K in sugarcane leaf tissues (Clements, 1957, 1964a, 1980).

C. Diagnosis and Recommendation Integrated System

All methods described thus far use the critical level approach to interpret the crop's nutritional status. However, Beaufils (1973) and Beaufils and Sumner (1976) have introduced a totally different concept to plant tissue analysis. Their concept is to use ratios of tissue nutrient concentrations to calculate indices for diagnosis of deficiencies and imbalances. This technique is called the Diagnosis and Recommendation Integrated System (DRIS) (Beaufils, 1973; Beaufils & Sumner, 1976).

The advantages of DRIS are many, according to its developers (Beaufils, 1973; Beaufils & Sumner, 1976; Sumner, 1979). Briefly stated, DRIS interrelates all plant, soil, and environmental factors, and the effect of each upon crop yield. It is irrelevant to users of DRIS whether any specific factor is known to have an effect upon yield. All factors are considered, based upon the premise that any specific factor could become limiting under certain currently undefined conditions.

An index, as a function of yield, is derived for each cultural and environmental factor (Beaufils, 1973; Sumner & Beaufils, 1979). The more negative an index value for a nutritional parameter is, the more that nutrient is limiting crop yield. These indices also permit the ranking of yield-limiting factors in order of their effect upon crop yield.

Jones and Bowen (1981) compared crop logging with DRIS under a wide range of conditions in Hawaii. They found that the latter provided 3 to 5% fewer incorrect diagnoses of nutrient insufficiencies. Thus, DRIS may slightly improve diagnostic accuracy, but this benefit must be weighed against the complexities of DRIS, and the time required to learn the technique and interpret the data.

III. CROP LOGGING

The remainder of this discussion shall be focused on crop logging because this method of tissue analysis has played such a prominent role in the Hawaiian sugarcane industry for more than 40 yr. And, since Hawaii's cane sugar industry leads the world's producers in terms of yields every year (Blume, 1985; Smith, 1978; USDA, 1987). Crop logging can also be said to have had a major impact on world sugar production as well. Further, crop logging is used extensively in those areas that historically have produced the greatest yields of cane and sugar. Indeed, the introduction of crop logging coincides with these sharp increases in yields.

Remember, crop logging was originally developed for a 24-mo sugarcane crop and has subsequently been adapted to 12-mo crops in some areas. These adaptations also will be discussed where appropriate.

Portions of a completed crop log sheet for a 24-mo crop in an unirrigated field are shown in Fig. 17-1, 17-2, 17-3, and 17-4. The top section of Fig. 17-1 is a record of average maximum and minimum daily temperatures in degrees Fahrenheit, and also of sunlight in ($\text{g cal/cm}^2/\text{d}$). These data are

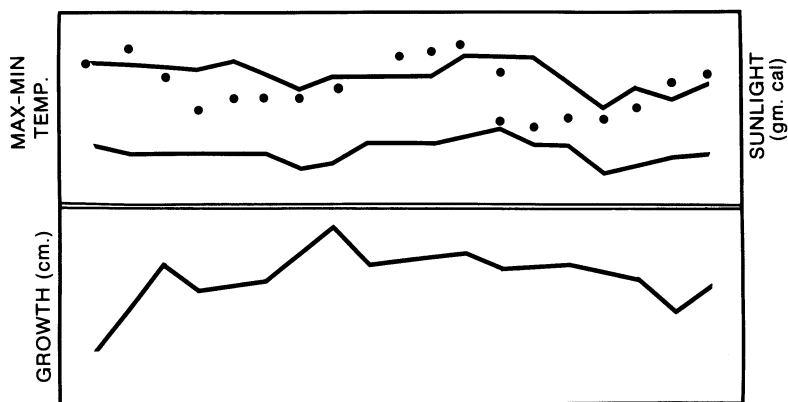


Fig. 17-1. A completed crop log for a 24-mo, unirrigated sugarcane crop in Hawaii. The lower bottom curve depicts crop growth as manifested by fresh weight of the stalks, in grams. The top and middle curves show maximum and minimum daily temperatures, respectively.

for record purposes only, though, because the grower obviously cannot alter either temperature or sunlight.

The lower section of Fig. 17-1 shows crop growth; i.e., total fresh weight in grams of sheaths 3, 4, 5, and 6, divided by five (five plants per sample). Some growers prefer to measure stalk elongation and, in that case, those data are recorded here instead of the fresh weights.

Actual leaf blade N contents (expressed as percentage of dry wt.) are recorded next and are shown as points connected by a solid line (Fig. 17-2). The "x's" are the normal nitrogen index (NNI) values. The NNI is the N level in leaf blade tissues from a previously high-yielding crop whose age and moisture content were identical to those of the present sample.

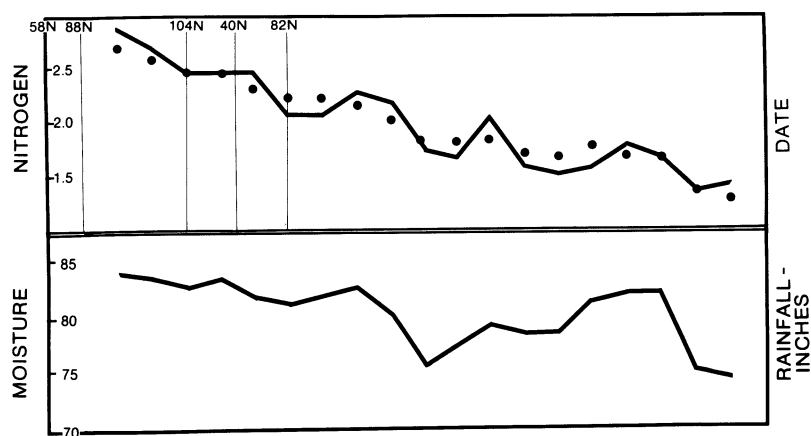


Fig. 17-2. A completed crop log for a 24-mo, unirrigated sugarcane crop in Hawaii. Actual leaf blade N contents (expressed as percentage of dry wt.) are recorded in the upper section and are shown as points connected by a solid line. The "dots" are the NNI values. The NNI is the N level in leaf blade tissues from a previously high-yielding crop whose age and moisture content were identical to those of the present sample. The sheath moisture content, expressed as percentage of fresh weight, is shown in the lower section.

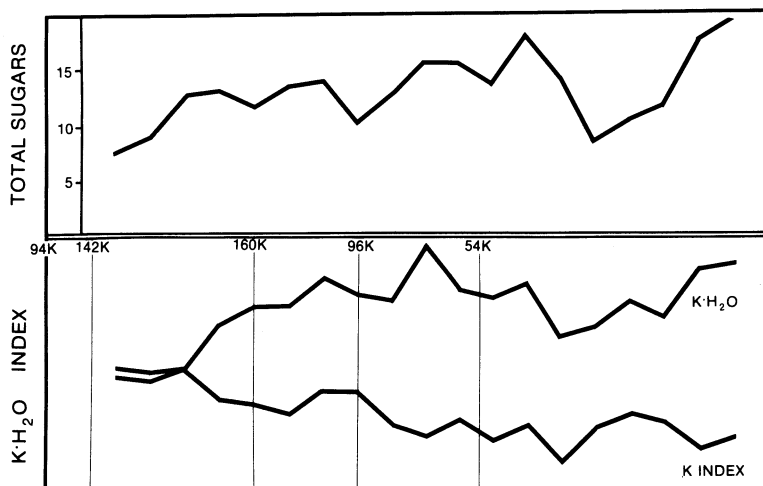


Fig. 17-3. The total soluble sugar content or “primary index” of the elongating leaf sheaths is shown in the top section of this portion of the crop log sheet. (Total soluble sugars = sugars in a water extract from the dried tissue, after inversion with invertase.) Sheath K contents are presented in the lower section as both the K index and the $K \cdot H_2O$ index. The K index is the K content of leaf sheaths [percentage soluble sugar-free (s-f) dry wt.]. Divide the y-axis values by 100 to obtain the actual K index value. The $K \cdot H_2O$ index is the K content of the sheaths expressed as a percentage of the tissue moisture and multiplied by 1000.

Actual crop age in months, measured from the date of planting or ratooning, and sampling dates are normally shown just above the N curves but these have been omitted from Fig. 17-2 to improve clarity. The numbers denote dates and amounts (in lb/acre) of N fertilizer applications.

The fourth section (the lower section in Fig. 17-2) records sheath moisture, rainfall, and irrigation applications if applicable.

The total soluble sugar content or primary index of the elongating leaf sheaths is shown in the next section (Fig. 17-3). (Total soluble sugars = sugars in a water extract from the dried tissue, after inversion with invertase.)

Sheath K contents are presented as both the K index and the $K \cdot H_2O$ index (Fig. 17-3). The K index is the K content of leaf sheaths [percentage soluble sugar-free (s-f) dry wt.]. Divide the y-axis values by 100 to obtain the actual K index value; e.g., a K index of 380 is actually 3.80% s-f dry wt.

The $K \cdot H_2O$ index is the K content of the sheaths expressed as a percentage of the tissue moisture and multiplied by 1000. Thus, a $K \cdot H_2O$ index of 425 is actually 0.425. The $K \cdot H_2O$ index, like that for N, is quite complex. It, too, will be discussed later.

All data in the lower left section of Fig. 17-4 are obtained from the boom stage samples taken when the cane is 8- to 12-mo old.

Three different P indices are used in crop logging; i.e., the standardized phosphorus index (SPI), the Fifth Internode P content, and the amplified phosphorus index (API). The calculation and application of these will be discussed later also.

OTHER ELEMENTS INDEX YR S 0.268 0.291 0.281 84 Zn 32 24 29 84 Cu 11 14 14 84 B 2.2 2.2 2.4 84 Al 8 5 7 84 Mo 1.6 1.6 1.2 84				FERTILIZATION LBS/A N P K PLAN 340 200 510 ACT 138 218 236 ACT 242 396 ACT 282 492 ACT 364 546 ACT			
Date 4/14 6/2 7/15 SPI .081 .077 .083 5th .037 .042 .036 API 29.97 32.34 29.44 Ca 0.24 0.27 0.28 Mg 0.10 0.14 0.11 Mn 72 92 111 % SiO 1.14 1.18 1.21 Mn/Si 63 78 92				IRRIG RND5 O TOTAL RAIN 195.1 TOTAL GM. CAL. 312.105 AVE. MIN. TEMP. LAST 3 MO. 64 AVE. MAX. TEMP. LAST 3 MO. 76 TOTAL DAY DEGREES			
HARVEST RESULTS THIS CROP LAST YR. RECORD VARIETY 3775 3775 49.5 YEAR 1985 1983 19.67 AGE 24.1 22.0 23.8 TCA 110.4 106.0 116.2 TCTS 9.32 9.11 9.44 TSA 11.84 11.63 12.31 TSAM TPA 0.387 0.529 0.517 1st Expr. 13.24 13.07 13.90 BRIX 20.6 20.4 20.9 POL 18.7 18.4 19.0 PURITY 90.8 90.1 91.1				FIELD DATA DATE STARTED April 20. 1983 SCHED HARV April 16. 1985 DATE HARV April 24. 1985 LEAF N AT HARV 1.39 SHT MOIST. AT HARV 77.9 REMARKS STAND AT 6 MO Excellent HARV METHOD Push Rake SOIL TYPE Hydrol Humic SCHED HARV MO APRIL DATE HARV'D April 24. 1985			
FIELD 104 AREA 12.3 pH 5.4 SOIL TYPE Hydrol Humic PLANTATION VARIETY H59-3775 CYCLE Plant CROP YEAR 1985 ELEVATION 350-425							

Fig. 17-4. This section of the crop log sheet contains data on micronutrient concentrations in the sheaths of "boom-stage" samples, planned and actual fertilizer applications, field data pertaining to cultural practices, and a historical record of yields from that field.

Calcium and Mg contents of the elongating sheaths, as percentages of the soluble s-f dry wt., are also shown in this lower left section. Comparison of actual Ca and Mg levels with the critical levels (Table 17-1) will guide your decision whether to apply these nutrients to the growing crop or to wait until the next crop is established.

The S content of the sheaths is reported as percentage s-f dry wt.; concentrations of other micronutrients are in mg/kg s-f dry wt., or ppm.

If the tissue level falls below the critical level for one or more of the micronutrients (Table 17-1), the usual practice would be to incorporate the

Table 17-1. Comparison of critical levels of micronutrients in elongating leaf sheaths of sugarcane (Clements, 1980; Bowen, 1983).

Nutrient	Critical level in elongating sheaths		
	Clements	Bowen	
		TCH†	TSH†
Ca‡	0.17	0.20-0.25	0.20
Mg‡	0.08	0.10	0.10
S‡	0.22	0.30	0.30
B§	2.0	2.0	2.0
Zn§	10	10	10
Cu§	10	5	8
Mn§	10	10	10
Si‡	--	2.20	--
Mn/Si₂¶	--	--	50

† TCH = tonnes cane per hectare; TSH = tonnes sugar per hectare.

‡ Percent soluble sugar-free dry wt.

§ Soluble sugar-free dry wt. (mg/kg).

¶ Mn (mg/kg s-f dry wt.)/SiO₂ (percentage s-f dry wt.).

appropriate fertilizer into the soil when the next crop is started. Rarely is a micronutrient fertilizer applied to a growing crop. The most frequent exception to this, however, is S that can indeed be applied successfully to established crops.

The Mn/SiO₂ ratio is accorded great significance in crop logging. Although SiO₂ is not known to be essential for sugarcane, it can often alleviate Mn toxicity.

Certain elements essential to optimal growth and development of sugarcane are sometimes present in soil in excessive quantities and are thus toxic to the plants. This is most likely to be a problem with micronutrients; e.g., B and Mn, but maximum levels of tolerance have yet to be established.

Still other elements are not essential but are nevertheless markedly toxic; e.g., Al, the concentration of which in the sheaths is given in the "Other Element Index" section of Fig. 17-4. This, too, is expressed in mg/kg s-f dry wt. or ppm.

Fertilization data for N, P, and K, both planned application rates and the actual amounts applied, are reported in the "Fertilizer Lb/A" section. The actual values shown for N and K should agree with the totals that can be obtained from the N and K sections of the crop log above. All phosphate fertilizer is applied at the start of the crop, though, so the quantity of phosphate shown in this section represents a single application at the time of planting or ratooning.

There is also space in this section for a summary of total rainfall received and irrigation rounds applied (if any) during the crop; total (g cal)/m² of light received; average minimum and maximum daily temperatures for the last 3 mo prior to harvest; and total "day-degrees."

The concept of "day-degree" requires some explanation. It is defined as the excess of degrees (in °F) more than 70 °F each day. Thus, if the maxi-

imum temperature for a given day was 82 °F, then 12 “day-degrees” would be recorded.

Miscellaneous field cultivation and harvest data are given in the “Field Data” section (Fig. 17-4). These data are part of the complete crop record and also contribute to an accurate interpretation of the tissue analysis data.

The lower left section headed “Harvest Results” (Fig. 17-4) contains information on various yield parameters from the current crop, the preceding crop and the record-yielding crop from that field.

Other pertinent data are recorded at the extreme bottom of the crop log sheet; i.e., field number, elevation and area; variety or cultivar being grown; soil type and pH; and crop cycle (plant, first ratoon, and second ratoon).

Crop logging, when applied to a 24-mo crop, permits correction of N and K deficiencies at any time until the crop reaches an age of 14 mo. No fertilizer is applied after this point in the crop cycle because it interferes with proper crop ripening. To alleviate this limitation on the applicability of crop logging, Sund and Clements (1974) recommended that samples be taken at 14-d intervals when working with a 12-mo crop. The sampling procedure was not modified, though.

Many regions in which sugarcane is grown as a 12-mo crop are characterized by saline soils and drought. Water table variations are often shown on crop logs to warn the grower of impending problems with salinity. Salinity is the most dominant negative growth factor in these areas and is thus monitored closely (Sund & Clements, 1974).

The sheath moisture level is regarded as the single most useful index in many regions (Sund & Clements, 1974). In recognition of this fact, these data are plotted for the 12-mo crop, along with normal moisture levels for the cultivar being grown. The normal moisture level is defined as the sheath moisture level at the same age in excellent crops, expressed as a percentage of fresh weight.

Experience has taught that sheath moisture, and tissue N and P concentrations are the factors most likely to pose problems for the cane farmer in areas where crop logging has been adapted to the 12-mo crop (Sund & Clements, 1974). Therefore, these parameters are measured biweekly while other nutrient levels are analyzed only occasionally.

A. Data Interpretation

Inherent to proper interpretation of any tissue analysis data is a thorough knowledge of the amount of each nutrient that must be present in the cane tissues at any given stage of growth if maximum yields are to be obtained; i.e., the critical level for each nutrient. The concentration of each nutrient in the index tissue (elongating sheaths in crop logging) is measured and compared with its concentration in samples from the highest-yielding fields *cultivated under the same conditions*. The latter is important; data obtained under different environmental or cultivation conditions cannot be compared accurately.

This standard of comparison obtained from tissue samples from the highest-yielding fields is the critical level for that nutrient. It is presumed that the nutrient concentrations in tissues from record-yielding fields will be those that must be maintained in subsequent crops in those fields if similar high yields are to be obtained (Clements et al., 1952; Clements, 1980). If the nutrient concentration selected as the critical level is not accurately correlated with the highest-yielding crops, then the standard of comparison is incorrect for future crops; i.e., future yields will be less than the maximum previously realized.

Critical levels for seven essential micronutrients, for apparently nonessential but beneficial Si, and for the Mn/SiO₂ ratio are presented in Table 17-1 (Bowen, 1983; Clements, 1967, 1980; Clements et al., 1974). The critical levels are virtually the same whether one uses tonnes cane per hectare (TCH) or tonnes sugar per hectare (TSH) except in the case of Cu. A tissue concentration of 5 mg Cu/kg s-f dry wt. is associated with maximum cane tonnage but 8 mg Cu/kg s-f dry wt. is required to produce maximum sugar yields. Cane yields decrease as the Cu content of the sheaths increases above 5 mg/kg so maximum sugar production is achieved at a point where cane tonnage is actually less than the maximum. In these experiments, the tonnes cane/tonnes sugar (TCTS) ratio was 10.11 when the sheath Cu content was 5 mg/kg. At a sheath Cu content of 8 mg/kg when sugar production was maximal, the TCTS ratio dropped to a desirable 6.59 (Bowen, 1983).

Much progress has been made in understanding critical levels since 1980. We now know, for instance, that myriad factors bear upon critical levels and tissue nutrient concentrations in addition to nutrient availability in the rhizosphere per se. Crop age and tissue moisture content strongly influence the critical levels for N and K, so much so in fact that these parameters must be considered in every interpretation and application of an N or K analysis (Clements, 1980).

Clements (1980) showed that climatic and ecological factors influence N uptake and accumulation in sugarcane tissues. The significance of these effects is so great that they preclude detection of a direct correlation between N availability in the soil, tissues N levels, and yield. This absence of direct correlations among these parameters may seem initially to be a failure of tissue analysis. However, Clements (1957, 1959, 1980; Clements & Moriguchi, 1942) used this situation to demonstrate that factors other than nutrient availability influence uptake and accumulation. The concept of the standardized N index (SNI) arose from this early work.

Six factors, other than availability, were shown to affect the accumulation of N in sugarcane: sheath moisture content, crop or plant age, minimum and maximum daily temperatures, soil moisture content and light intensity/duration. These six factors account for almost 70% of the variability in tissue N levels without the available N being included (Clements, 1957, 1980; Clements & Moriguchi, 1942; Clements et al., 1952).

Clements et al. (1952) hypothesized that the interpretation of tissue N contents could be greatly facilitated if a relatively simple mathematical equa-

tion could be derived to standardize tissue N levels for all conditions under which sugarcane is grown.

Further statistical analysis of crop log data showed that, of the six factors affecting tissue N contents listed above, the dominant two were crop or plant age at sampling and sheath moisture contents. This discovery led to the derivation of a regression equation for the normal nitrogen index (NNI).

The NNI values are calculated with this equation from previous data obtained locally from high-yielding crops. A table is constructed that includes all possible sheath moisture values between 73 and 90%, at intervals of 0.5%. Crop ages in the range of 2 to 28 mo are included, at intervals of 0.5 mo. The theoretical N content of the elongating leaf blades is entered into the table for every combination of sheath moisture and crop age. These tabular N values are called the NNI values because they represent the tissue N content that must be maintained at any given combination of sheath moisture and crop age if yields similar to the earlier record ones are to be obtained.

The actual N content of a particular sample whose age and sheath moisture content are already known is compared to the NNI value from the table. The actual N content should be close to the NNI value. Excess actual N means that fertilizer has been applied injudiciously and that it may not be possible to "ripen" the cane properly. An actual N content below the NNI value indicates that the crop has inadequate N available and that fertilization is likely needed (Clements, 1980; Clements et al., 1952).

The concentration of K in the leaf sheaths, like that of N in the blades, is also affected by factors other than K availability in the soil. Using multiple regression analyses, Clements (1959, 1970, 1980) showed that the single most important factor influencing K accumulation in the elongating sheaths was sheath moisture content. There was no statistically significant correlation between the actual sheath K contents expressed as a percentage of the s-f dry wt. and the ultimate crop yield. However, when these same K contents were expressed as a percentage of the sheath moisture, a very meaningful relationship between K levels and ultimate crop yield was apparent.

The $K \cdot H_2O$ index is calculated with this equation:

$$K \cdot H_2O \text{ index} = \frac{[(K, \%s\text{-}f \text{ dry wt.})(100 - \%sheath \text{ moisture})]}{\%sheath \text{ moisture}} .$$

Calculation and application of $K \cdot H_2O$ values are expedited by using a table of pre-calculated values. $K \cdot H_2O$ index values are tabulated for all possible combinations of sheath moistures from 73 to 90%, at 0.5% intervals, and actual tissue K contents ranging from 1.1 to 3.0% s-f dry wt. A $K \cdot H_2O$ index value of 0.425 is normal under most conditions. (In actual practice, the $K \cdot H_2O$ index values are usually multiplied by 1000. Thus, 0.425 would be reported as 425.) Above 0.425, too much K is present and below this index value, inadequate K is available.

Phosphorus accumulation depends upon factors other than P availability (Clements, 1955, 1958, 1980) and requires use of three separate P indices.

Analyses for P are run on the elongating leaf sheath samples and also on the fifth internode samples. The latter is obtained from the fifth internode of the stalk below the point of attachment of the oldest living leaf (Clements, 1958; Clements & Ghotb, 1969).

A standard phosphorus index (SPI) value is calculated using the P content of the sheath samples (percentage s-f dry wt.), the sheath moisture content and the total soluble sugar content of the sheath sample. This SPI value is compared to the SPI value calculated for an assumed moisture content of 81.0% and total sugar content of 10.2%.

Later work by Clements (1955, 1958, 1980) showed that yet another parameter more accurately portrayed the P status of the crop; i.e., the amplified phosphorus index (API):

$$\text{API} = (\text{SPI}) \times (\text{5th internode P})$$

after both the SPI and 5th internode P values have been converted to whole numbers.

The API has consistently proven to be the most useful of the three P indices in assessing the P nutritional status of the crop (Clements, 1958, 1980). Optimal API values vary between plant and ratoon crops. However, 3200 or more is generally considered sufficient for a plant crop and 3600 or greater for a ratoon. The API values are used as guides for phosphate requirements for the next crop only, however. All phosphate is applied at the time of planting or ratooning in Hawaii so there is no opportunity to correct a P insufficiency during the crop cycle.

B. Other Factors Affecting Interpretation

Nitrogen, P, and K are not the only essential nutrients whose uptake and accumulation depend heavily upon factors other than their respective availabilities in the soil, though. Micronutrient accumulation in the elongating sheaths strongly depends upon crop age at the time of sampling, for example (Bowen, 1975).

Sheath Ca and Mg concentrations correlate negatively and nonlinearly with age. Copper and B accumulations are not affected by crop age, however. Thus, the importance of sampling elongating sheaths, or other tissues as the case may be, that are the same age physiologically becomes very obvious, at least for Ca and Mg.

Sugarcane cultivars vary widely in the amounts of essential nutrients required for optimal growth and maximal yields (Bowen, 1973a). Thus, a critical level is not likely to be applicable to all cultivars under all conditions (Table 17-2).

Consider Zn as an example. Cultivar H53-263 requires much less Zn for optimal growth than does cv. H57-5174. The latter readily develops symptoms of Zn deficiency in the field whereas the former rarely does so. Research has revealed that cv. H53-263 roots have a sixfold greater affinity for Zn than those of cv. H57-5174 (Bowen, 1973a). Thus, cv. H53-263 can use the

Table 17-2. Critical levels for micronutrients in three Hawaiian sugarcane cultivars (Bowen, 1983). (TSH used as the yield parameter.)†

Nutrient	H59-3775	Cv. H49-5	H53-263
Ca‡	0.20	0.22	0.22
Mg‡	0.10	0.10	0.10
S‡	0.27	0.30	0.30
B§	2.0	2.0	2.0
Zn§	10.0	10.0	7.0
Cu§	7.5	8.0	8.0
Mn§	10.0	10.0	10.0
Mn/SiO ₂ ¶	50-75	50-75	50-75

† TSH = tonnes sugar per hectare.

‡ Percent soluble sugar-free dry wt.

§ Soluble sugar-free dry wt. (mg/kg).

¶ Mn (mg/kg s-f dry wt.)/SiO₂ (percentage s-f dry wt.).

Zn that is available more efficiently than H57-5174. This explains, at least in part, why H53-263 can thrive under conditions that would be Zn-deficient for H57-5174 (Bowen, 1973a). Similar differences among cultivars of sugarcane have been found for other essential nutrients (e.g., N and Fe) (Clements, 1980).

Both synergistic and antagonistic interactions between essential nutrients affect their uptake, translocation, and utilization in plant tissues, and therefore affect interpretation of tissue analysis data (Bowen, 1973a, 1983). These problems are especially serious with micronutrients.

For example, synergistic interactions have been observed in the uptake of Ca-S, Ca-Zn, Ca-Cu, Ca-B, Mg-S, Mg-Zn, S-Zn, S-Cu, S-B, S-Mn, Zn-B, and Cu-B (Bowen, 1981). Antagonistic interactions were found between Ca-Mn, Mg-Cu, Mg-B, and Zn-Cu (Bowen, 1981). Thus, a low tissue content of Cu, for instance, may not indicate inadequate Cu availability. Rather, it may mean that excessive Zn is present in the soil, thus interfering with uptake and accumulation of Cu in the sheath tissues.

Silicon is a seemingly nonessential nutrient for sugarcane (Clements, 1967; Clements et al., 1974), although this fact has certainly not been unequivocally established (Elawad et al., 1982, b; Gascho, 1978; Gascho & Andreis, 1974). Silicon does significantly increase accumulation of S and Mg and decrease that of Mn, Cu, and B under some conditions, however (Bowen, 1981; Clements, 1980). Again, an apparent deficiency of Mn or Cu, for example, may indicate high SiO₂ levels in the soil, not Mn or Cu deficiency per se (Clements, 1967; Clements et al., 1974).

IV. TOXICITIES

Toxicities of essential nutrients are now receiving much attention from researchers, particularly micronutrient toxicities (Bowen, 1983). Boron, Cu, and Mn, for example, are markedly toxic to sugarcane and to many other plants when available in excess. There is often a narrow margin between suffi-

ciency and toxicity for B. The critical level for B in elongating sheaths is 2.0 mg B/kg s-f dry wt. Increasing the tissue B level to 3.0 mg/kg s-f dry wt. decreases sugar tonnage by 24% (Bowen, 1970, 1983).

Toxicities occur with other essential nutrients also. Sulfur, for example, has a critical level of 0.30% s-f dry wt. If the sheath S level increases to 0.35% significant decreases in both cane and sugar tonnages are likely to occur (Bowen, 1983).

Excess available N also has a negative effect on sugar yield. One means used to properly "ripen" sugarcane is to induce a N stress or deficiency. When the plant is thus stressed, vegetative growth ceases and sugar rapidly accumulates. If too much N is available during this ripening phase of the crop cycle, though, sugarcane will continue to grow vegetatively at the expense of sugar accumulation in the stalks (Clements, 1959, 1980). This situation is not a true toxicity but the result for the grower is still lower sugar yields.

Nutrient excesses are readily controlled in those cases where the excess is caused by overfertilization. Close monitoring and accurate interpretation of tissue analysis data will assist you in determining the correct amounts of fertilizer to apply as well as the optimum time to apply it.

The toxicity problem is considerably more severe when a micronutrient is naturally present in the soil in amounts detrimental to sugarcane growth. Liming to increase the soil pH is one possible way to render some micronutrients less readily available and thus to lower the tissue concentrations.

Antagonistic interactions may also offer a possible solution to specific problems. For instance, a moderate application of Cu would decrease tissue Zn levels.

A long-range solution to an inherent soil toxicity is the selection of sugarcane cultivars that can tolerate the excess nutrient in question. This is currently an active research field for many crops in the tropics and subtropics. If it is too expensive or otherwise not feasible to correct a detrimental soil condition, the alternative is to modify the crop genetically so that it can adapt to the adverse soil condition.

V. PRACTICAL APPLICATION OF SUGARCANE TISSUE ANALYSIS METHODS

Regardless of just what measures you take to optimize the nutritional status of the sugarcane crop, do not overlook the fact that maximal yields ultimately depend upon a balanced supply of the 17 currently recognized essential nutrients. (It was suggested in 1972 that chlorine be added to this list of essential nutrients for sugarcane [Bowen].) Maintenance of this balance can be greatly facilitated by plant tissue analysis but numerous pitfalls await the unwary practitioner (Bowen, 1978).

Think of plant tissue analysis in terms of two separate operations: (i) sampling of crop fields and preparation of the plant material for the labora-

tory, and (ii) chemical analysis of the plant material. The latter will usually be done by an independent laboratory and thus will be beyond your control. So, we will concentrate upon the former to make certain that preventable error is not creeping into your results and costing you money through lowered yields or excessive fertilization.

The most critical step in successful crop control through plant tissue analysis is the selection of an index tissue for each nutrient. What tissue are you going to sample? Use one of the established methods such as crop logging or a modified TVD method to avoid this problem.

Critical levels also must be determined accurately before you can expect meaningful results from plant tissue analysis. Again, this has already been done for you if you use one of the established methods.

Let me inject a note of caution here, however. Insufficient concentrations of a specific nutrient in the tissue do not necessarily mean that inadequate amounts of that nutrient are present in the soil. For example, poor root development due to disease, nematodes, insects, or chemical toxicities can manifest itself in reduced nutrient uptake. Therefore, when the nutrient contents of the index tissue drop below the critical levels, the reasons for this should be investigated before any corrective action is taken.

In the field, the weakest link in the tissue analysis procedural chain is selection of the plants to be sampled, both in regards to sites of the sampling stations within the field and the individual plants and stalks chosen. Improper technique at this stage means that subsequent chemical analyses and fertilizer recommendations will be inaccurate. Sampling, therefore, receives much care and attention.

Set forth a few general guidelines in regard to site selection. First, topography or terrain is a major determinant. A uniform field requires fewer sampling stations than does a field dominated by steep slopes, inadequately drained areas and rocky outcroppings. Second, mixed cultivars within a field can necessitate multiple sampling sites because sugarcane cultivars manifest nutritional variabilities. Third, if the date of planting differs significantly in different parts of the field, at least one sample should be taken for each plant age. Lastly, areas of a field that historically show poor growth and low yields, regardless of the reason, should be sampled separately.

We could list numerous other variables that would require separate sampling sites or a smaller area per site. Rather than do that, sample site selection should be done by an experienced person who has detailed knowledge of the field in question.

It is not practical to offer guidelines as to how large an area a single sample site can represent because there are simply too many variables involved. Perhaps it might be useful to mention that one sample station per 10 ha is common in a uniform cane field. Avoid field edges and irrigation ditches when taking plant tissue samples to minimize "edge effects" so familiar to statisticians.

Although there is some disagreement about the need for doing this, take your plant samples within 3 h after sunrise to avoid possible diurnal fluctuations in moisture and nutrient composition. Tissue levels of N and K, for

example, are significantly affected by tissue moisture contents as discussed above.

The practical importance of early morning sampling has not been sufficiently evaluated experimentally to prove that it is necessary. But, to be safe, sampling should continue to be done early in the day until it is shown to be unnecessary.

If a lengthy time delay is anticipated between sampling and return of the tissue to the laboratory for fresh weight determinations, seal the cut material in plastic bags to retard moisture loss.

After the plant material has been cut, it must be cleaned, dried, and prepared for chemical analysis. These steps also involve several potential pitfalls. First, surface contaminants such as loose soil and dusts are removed by shaking the sample.

Next, cleaning is needed. One method is to wash the sample quickly in flowing tap water with gentle scrubbing to loosen adherent surface films, and then pass the tissue through a dilute phosphate-free soap solution. The importance of using phosphate-free soap is obvious if reliable P analyses are to be run. Finally, the tissue is rinsed in distilled water and blotted dry.

Actually, the best method for cleaning tissue surfaces is widely debated among tissue analysis practitioners. Recommendations vary from the washing just described, to brushing samples individually with a camel hair brush, to wiping with a damp cloth. Wiping alone is clearly quite insufficient for removing contaminants from sugarcane blades and sheaths, though.

Failure to remove dusts, soil, and pesticide residues will likely have little effect upon apparent N, P, and K concentrations in the sample, but these contaminants will cause erroneously high micronutrient levels.

On the other hand, excessive washing can also introduce error because K and other highly soluble nutrients can be leached from the tissue. Losses of K from sugarcane sheaths are commonly <2% under the washing regime outlined above, though.

Sugarcane tissues should be quickly dried after sampling to minimize physical and biochemical changes that would affect the accuracy of the analytical data. For example, respiration continues in tissue samples after they have been cut from the plant until they are dried. Since respiratory enzymes convert sugars to CO₂ and water, failure to dry samples promptly can cause a loss in their weights and sugar contents. Also, protein metabolism is altered in collected samples. This may lead to false N readings.

The drying temperature must be sufficiently high to destroy enzymes, but not so high as to cause tissue loss by burning and charring. Overnight drying in a forced draft oven at 70 to 75 °C works well.

It is unlikely that all moisture is removed even under these conditions, however, so the “dry weight” of the sample is probably not really that at all. Some water will be retained because it is difficult, if not impossible, to remove it all without destroying some of the tissue with high heat. Although the samples are not actually being dried completely, we hopefully are drying them to a *constant* moisture content. Continue to refer to the tissue as being “dried,” to avoid confusion.

The dried tissue is then normally delivered to the laboratory for chemical analysis. The data are most useful to the grower if he receives it within a few days after sampling. A short "in-laboratory" time permits the farmer to use the data to correct deficiencies in the growing crop; e.g., to apply N fertilizer if the actual N level falls below the NNI value.

Some sources of potential error in the sampling process have been suggested. There are also many such sources in the analytical and interpretive phases of tissue analysis, just as there are in making decisions about necessary measures to correct nutritional problems that are detected. Numerous research projects throughout the sugarcane-growing regions of the world are currently being addressed toward elucidating the optimal procedures for applying plant tissue analysis to this crop.

Sugarcane tissue analysis is a dynamic area of research and application. Thus, it behooves the user to be alert for changes and updates in the analytical and interpretive procedures.

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Chapter 18

Plant Analysis as an Aid in Fertilizing Cotton¹

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The vegetative and reproductive growth patterns of cotton (*Gossypium hirsutum* L.) are readily adapted to plant analysis. The indeterminate growth pattern over a relatively long growing season allows plant analysis to be used for nutritional studies, monitoring of selected plant parts, and corrective fertilization for observed deficiencies during the growing season.

I. NUTRIENT UPTAKE PATTERNS

A. Dry Matter Accumulation

It is essential to understand the growth and mineral uptake patterns of a specific crop prior to interpreting plant analysis data. Not only do species differ, but there are also varietal and locality differences. The two main cotton-growing areas of the USA are the irrigated dryland areas of the Southwest Great Plains and the humid areas of the Southeast. These regions represent a range of climatic, varietal, and soil differences that are reflected in growth and nutrient uptake.

Research in Georgia (Olson & Bledsoe, 1942) and California (Bassett et al., 1970) showed similarities as well as contrasts in the pattern of dry matter production and nutrient uptake. In both areas, a slow rate of early growth was followed by a period of rapid increase in dry matter production and nutrient uptake. Dry matter production in Georgia was 3.1, 8.0, 37.6, and 51.2% of the total producing during the planting to seedling, seedling to early square, early square to early boll, and early boll to maturity stages, respectively. Under California conditions, cotton planted on 1 April produced 2 to 4% of the total dry matter at first square, an additional 7 to 10% by first

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flower on 25 June and a further 66% during the 6-wk period between 1 July and 15 August. Cotton in irrigated areas grew proportionally more in the later growth stages than did cotton in non-irrigated areas.

Figure 18-1 (Halvey, 1976) represented the dry matter accumulation by aboveground/aerial plant parts during a growing season. Under the irrigated conditions, the growth period between full flower (72 d) and boll opening (112 d) accumulated 75% of the total dry matter. This sigmoidal pattern of growth was also reported by Bassett et al. (1970).

Wanjura and Sunderman (1976) reported that dry matter accumulation on a per plant basis was greater in a 100-cm row width than a 25-cm row width. However, the accumulation on a per unit area basis was greater for the narrower row width. They also reported that an increase in N rates reduced the vegetative dry matter loss from peak bloom to maturity. Gardener and Tucker (1967) indicated that development of vegetative plant parts was reduced by early season N deficiency especially under a one-peak flowering period. However, under an elongated two-peak flowering period, an early season N deficiency can be compensated by an adequate supply of N during

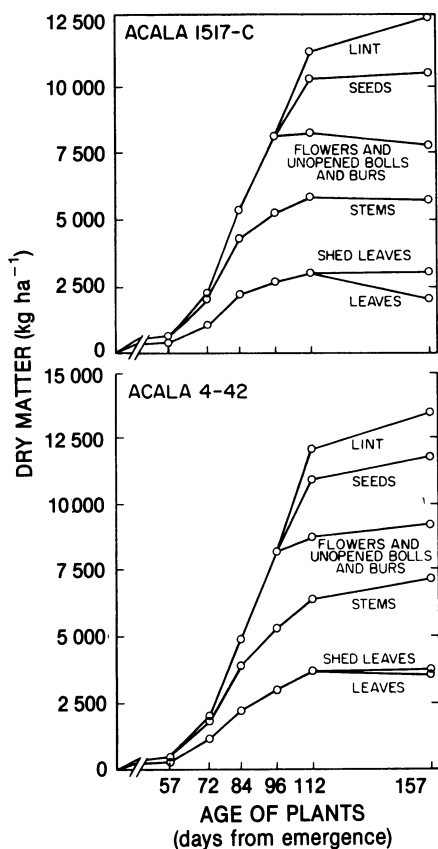


Fig. 18-1. Accumulation of dry matter in the aerial plant parts of cotton cv. Acala 1517-C and Acala 4-42 (Halvey, 1976).

the late season. Koli and Morrill (1976) observed both a prolonged vegetative growth period and fruiting period when a fertilizer rate of 45 kg of N ha⁻¹ was compared to 0 kg of N ha⁻¹.

B. Nutrient Accumulation

1. Total Uptake

In general, early season nutrient uptake by cotton proceeded more rapidly than dry matter production. Cotton grown under irrigation absorbed about 15% of the total N, P, and K while dry matter accumulation was <10% of the total accumulated (Bassett et al., 1970). In humid areas, cotton absorbed 22 and 30% of the total N and K, respectively, during the accumulation of about 11% of the total dry matter (Olson & Bledsoe, 1942).

A comprehensive study on the seasonal uptake of N, P, and K among plant parts is reported by Bassett et al. (1970). Table 18-1 shows a continuous uptake of these nutrients during the growing season, the quantities/amounts of these nutrients during the growing season, and the extent of their translocation from leaves and stems to the more metabolically active region of seed formation. The greatest changes in nutrient uptake occurred between 60 and 120 d after planting. Uptake of N, P, and K increased about 10-fold during this 60-d period.

Table 18-1. Uptake and distribution of N, P, and K in plant parts (Bassett et al., 1970).

	Average no. days after planting						
	60 15 June	75 1 July	90 15 July	105 1 Aug.	120 15 Aug.	135 1 Sept.	165 1 Oct.
	kg ha ⁻¹						
	<u>Nitrogen</u>						
Stems	1.0	3.8	7.1	9.9	12.7	12.1	18.3
Leaves	9.3	19.3	33.3	38.5	45.5	73.2	37.9
Burrs		(3.5)†	(14.5)†	(27.0)†	15.7	14.1	11.6
Seed					34.4	55.8	75.8
Total	10.3	26.6	54.9	75.4	108.3	119.2	143.6
	<u>Phosphorus</u>						
Stems	0.2	0.6	1.3	1.7	2.2	2.0	3.1
Leaves	1.1	1.7	3.2	3.8	3.9	3.4	3.6
Burrs		(0.5)†	(2.5)†	(4.6)†	.28	2.7	2.0
Seed					5.8	9.1	12.2
Total	1.3	2.8	7.0	10.1	14.7	17.2	20.9
	<u>Potassium</u>						
Stems	1.6	5.0	13.7	18.9	28.5	25.0	27.5
Leaves	5.7	12.1	22.4	29.8	31.4	25.2	20.6
Burrs		(1.3)†	(10.4)†	(22.3)†	25.4	44.4	52.5
Seed					13.0	17.0	20.6
Total	7.3	18.4	46.5	71.0	98.3	111.6	121.2

† Entire boll—includes burrs and seed.

Sabbe and Hansen (1983) reported that the total plant content of Zn, Fe, Mn, and Cu increased two- to threefold during the 7-wk period following first bloom. However, the rate of dry matter accumulation during this period was proportionally greater than the micronutrient uptake, thereby resulting in a decrease in micronutrient concentration among most plant parts.

2. Plant Parts

Correct selection of the proper plant part for the determination of the nutrition status of the whole plant requires an understanding of the partitioning within the plant as well as the seasonal distribution of specific nutrients.

A direct relationship exists between the leaf and petioles for the more mobile nutrients (i.e., N, P, and K); whereas, for the less-mobile nutrients the relationship are inversed especially for the top leaf and petiole at the later sampling dates (Table 18-2). Data in Table 18-2 indicate that the selection of a plant part must consider not only plant age but also the nutrient.

3. Nitrogen

Cotton requires N for both the vegetative and the reproductive phases of growth. Oosterhuis et al. (1983) demonstrated (Fig. 18-2) the pattern of N uptake and distribution in aboveground plant components. Their study demonstrated that the response to the initial rate of N increased N content in all plant parts. The N content increase was concomitant with a linear decrease in the N concentration of each plant part with time. This decrease in N concentration resulted from the rate of dry matter accumulation being

Table 18-2. Nutrient concentration of cotton plant parts at various sampling dates (Harris, 1960).

Date	Element	Whole plant	Top leaf	Top petiole	Bottom leaf	Bottom petiole
		g kg^{-1}				
29 June	N	43.5				
27 July	N		43.4	26.6	37.9	22.3
4 Aug.	N		45.7	24.2		
29 Aug.	N		37.3	10.5	24.4	8.9
29 June	P	5.1				
27 July	P		4.6	4.2	3.0	2.2
4 Aug.	P		4.5	4.2		
29 Aug.	P		3.1	1.9	2.5	1.4
29 June	K	20.8				
27 July	K		18.2	19.5	20.3	24.5
4 Aug.	K		12.6	19.9		
29 Aug.	K		6.9	17.1	16.4	27.5
29 June	Ca	15.1				
27 July	Ca		12.3	14.3	39.0	15.7
4 Aug.	Ca		12.3	12.7		
29 Aug.	Ca		17.0	8.9	33.7	12.2
29 June	Mg	4.0				
27 July	Mg		2.0	5.4	2.8	5.4
29 Aug.	Mg		5.0	2.4	1.7	2.5

greater than the N uptake. Wanjura and Sunderman (1976) obtained similar results for the leaves, stem, and fruiting bodies. Additionally, they found that the seed N concentration increased from peak bloom to maturity. These authors reported that plant N concentration did not differ between the 25- and 100-cm row spacings.

Thompson et al. (1976) tagged newly initiated leaves and fruit during early, middle, and late season to determine the N concentration among these age classes. The youngest leaves and fruits had initially higher N concentrations than later-appearing leaves and fruits. The N concentration of early

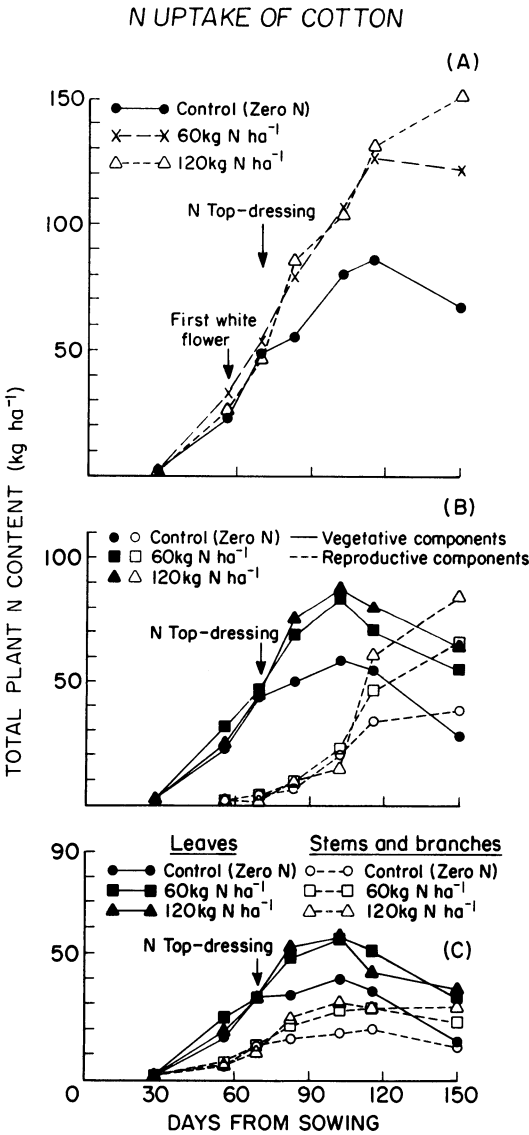


Fig. 18-2. Changes with age in aboveground N contents of total shoot, vegetative, and reproductive components of the cotton plant (Oosterhuis et al., 1983).

Table 18-3. Phosphorus concentration in cotton plant parts at various growth stages (Peacock, 1960).

Growth stage	Leaves	Petioles	Stems	Roots	Branches	Squares	Bolls
	g P kg^{-1}						
Four leaf stage	3.3	2.7	2.4	2.2			
Early bloom	3.5	2.2	2.1	1.5	2.9	4.4	
Early boll	2.7	1.7	1.6	1.5	1.5	4.9	3.7

season leaves decreased rapidly during their first 20 d; however, the leaves initiated later in the season did not decrease in N concentration during this first 20 d. Regardless of date of initiation, leaf ages between 20 and 40 d did not decrease in N concentration unless no N fertilizer had been applied. When N fertilizer had been applied the N concentration of fruits decreased for the first 40 d. In fruit older than 40 d, the N concentration remained constant. The authors concluded that the three phases of N utilization were: (i) rapid growth, (ii) photosynthetically active growth, and (iii) senescence. Therefore, a leaf would exhibit a rapid increase in N, level off, then decrease during senescence. However, if the leaf N concentration was low initially, it maintained a constant concentration until senescence.

4. Phosphorus

Patterns of P uptake and distribution among plant parts are similar to those of N (Halvey, 1976). As with N, the seed contained a high fraction of plant P at maturity (Basset et al., 1970). Phosphorus accumulation in the seed during formation was greater than total plant accumulation of P (Halvey, 1976). Data in Table 18-3 indicates the P concentration in plant organs during a growing season (Peacock, 1960). The peak translocation period for P occurred during the early boll development and may cause deficiency symptoms when other plant parts are marginally sufficient.

5. Potassium

There were two differences between the uptake pattern of K and those of N and P. The highest total plant accumulation occurred approximately at first boll opening and decreased slightly until maturity. The K in both the leaves and stems was translocated to the reproductive organs (Halvey, 1976). Hsu et al. (1978) reported that, although the rates of K decline in both leaf blades and petioles were dissimilar, each was a function of maturity and not a function of K fertilization rate. A constant decline in K occurred in leaf blades from early bloom to early boll; in petioles the early season decline was less than the decline from early bloom to early boll (Table 18-4). Apparently the bolls were greater sinks than flower buds.

6. Other Nutrients

Sabbe and Hansen (1983) observed a large increase in total Zn, Cu, Fe, and Mn during the reproductive stage (first bloom to 7 wk past first bloom).

Table 18-4. Potassium concentration of leaf-blades and petioles with stage of maturity (Hsu et al., 1978).

Plant part	Potassium concentration			Percentage decrease	
	Early square	Early bloom	Early half-grown boll	Early square to early bloom	Early bloom to early half-grown boll
	g K kg ⁻¹			%	
Apical immature blade	15.1	10.2	6.7	32	34
Young mature blade	12.5	10.7	7.8	14	27
Old mature blade	--	10.4	7.2	--	31
Apical immature petiole	39.6	38.0	28.1	4	26
Young mature petiole	33.1	26.6	10.9	20	59
Old mature petiole	--	25.5	10.6	--	58

However, the increases were less than the dry weight accumulation, thereby causing a concentration decrease during this growth stage. The exception was an increase in leaf Fe and Mn concentration at 7 wk past first bloom. The majority of the plant Fe and Mn were in the leaf; whereas, the majority of the Cu and Zn were in the fruiting tissue.

In four cotton cultivars and one cotton hybrid studied by Bhatt and Apukuttan (1982) the leaves, stems, and roots of 10-d-old seedlings had the maximum Mn concentration of the six growth stages sampled. Thereafter, rapid decline in Mn occurred until the square stage (from 2200 to 302, 825 to 68, and 3300 to 275 mg kg⁻¹ for the leaf, stem, and root, respectively) followed by a period of rather constant Mn concentration from peak flowering until harvest (140, 16, and 30 mg of Mn kg⁻¹ at harvest for leaf, stem, and root, respectively).

7. Summary

Patterns for dry matter accumulation and nutrient uptake by cotton can be summarized as (i) an initially slow growth until first flower followed by (ii) a rapid increase in both dry matter and nutrient uptake during fruit development. During the latter period, translocation of nutrients occurs to the fruiting bodies (sinks). Of the total nutrients accumulated during the growth season, about 50% of the N, 50 to 70% of the P, and 16 to 20% of the K were recovered from the field at harvest. These rather high harvest values indicate the need for maintaining a healthy plant capable of season-long nutrient uptake. A model has been described for the N balance and the carbohydrate growth requirements (Jones et al., 1974). The N requirement was based on the growth allowed by the carbohydrate supply. The model depended upon the soil N supply, daily N absorption rate, and the concentration in each plant part.

II. FACTORS INFLUENCING NUTRIENT CONCENTRATION IN COTTON

The concentration of nutrients in cotton tissues is related to environmental factors that influence their uptake. Knowledge of how these factors affect uptake and concentration is important for proper interpretation of plant analysis.

A. Nitrogen

Nitrogen is the most important nutrient for cotton production, and its effectiveness is dependent upon the environment.

1. Soil Factors

Most researchers investigating N fertility of cotton have observed a decline in N concentration in vegetative tissues over time. This decline may be due to dilution or remobilization (Thompson et al., 1976) or depletion of soil N and reduced uptake (Maples et al., 1977). Research in Arizona has indicated that the decline could be reversed by N fertilization through a drip system (Pennington & Briggs, 1983). This observation supports the hypothesis that depletion of soil N leads to a decline in plant N concentration.

The level of N in soil affects N levels in cotton plants (Amer & Abuamin, 1969; Baker et al., 1972; Cope, 1984). However, Bassett et al. (1970) found that total N uptake was not effected by rate of N application (45 and 134 kg of N/ha). Grimes et al. (1973) reported that irrigation enhanced N uptake and that coarse-textured soils were less responsive to in-season applications than were fine-textured soils. Maples et al. (1977) also found that irrigation or rainfall may increase petiole NO_3 . Time of application was also investigated by MacKenzie et al. (1963), who found that petiole NO_3 responded to fertilizer applied in either July or August. Petiole NO_3 response was less to a July application (as the plants were entering cutout) than to a August application (as the plants were leaving cutout). Other research found that a mid-season application of N fertilizer had little effect on petiole NO_3 (Oosterhuis & Morris, 1979). The form of N used as a fertilizer has been investigated for its effect on petiole NO_3 concentration (Amer & Abuamin, 1969). Calcium nitrate was found to be the most effective, followed by $\text{NH}_4\text{-NO}_3$, then urea. Nitrogen volatilization was suggested as a reason for the relative efficiency of the fertilizers.

Soil salinity affects N uptake and growth of cotton. Work with cotton in solution culture (Pessarkli & Tucker, 1985) found a decrease in N uptake with cotton grown under high-salinity stress (-1.2 MPa) but an increase under mild-salinity stress (-0.4 MPa). These researchers also found that plant growth and dry matter production were influenced to a greater extent than was N uptake.

Spatial variability of soil and plant N levels has recently been investigated in a statistical fashion. Research in Arizona (Tabor et al., 1984) found that

neither soil nor petiole NO_3 were randomly distributed in a cotton field but were related to the direction of cultural practices such as irrigation and row orientation. In a companion paper (Tabor et al., 1985), petiole NO_3 was most closely related to soil texture (i.e., clay percentage) and poorly related to soil NO_3 . Thus, in order for sampling to be representative, samples should be collected as far apart from each other as possible and still within the defined statistical range yet not within the same row.

3. Plant Factors

Plant factors such as variety, plant part, and growth stage may affect nutrient concentration. The often cited work of Joham (1951) found the petiole of the most recently mature, fully expanded leaf to be the most appropriate tissue for nutrient analysis. The work of Tabor et al. (1984) has confirmed these results and has added that if the age of an individual petiole is questionable, it is best to sample the older one. Others have disagreed on the usefulness of petiole monitoring for N in cotton. Most of the disagreement has come from rainfed areas of the USA (Baker et al., 1972; Sunderman et al., 1979; Touchton et al., 1981). Work from Rhodesia (Zimbabwe) also concluded that petiole monitoring was not useful (Oosterhuis & Morris, 1979). These researchers were unable to consistently correlate yield and petiole NO_3 levels. Where a correlation existed, there was insufficient time to correct the N deficiency. Oosterhuis and Bate (1983) found that NO_3 reductase activity of the most recently mature, fully expanded sympodial leaf was a better indicator of N status than was petiole NO_3 . In trials that looked at the difference between petioles and blades of the most recently mature, fully expanded leaf, Zelinski (1986) compared leaf NO_3 , NH_4 , and total N levels as well as petiole NO_3 and NH_4 levels to lint yield. None of the leaf N measurements were related to yield, and petiole NO_3 was closely related in only one year out of two. Unpublished work by the same author (L.J. Zelinski, Univ. of California Farm Advisor, Fresno County) found no relationship between leaf amino N and yield.

Research not directly involved in N fertilization has provided information on the N levels in other cotton plant tissues and has shown that N levels in vegetative parts decline as the season progresses, whereas N levels in seeds increase (Bassett et al., 1970; Elmore et al., 1979; Oosterhuis et al., 1983). The work by Elmore et al. (1979) found that timing of N application (either 100% preplant or 50% preplant and 50% sidedressed, or 100% sidedressed) had no effect on final seed N concentration.

Petiole NO_3 concentrations have been found to decrease up the stem (Joham, 1951; Pennington et al., 1983; Woon, 1977). The work by Tabor et al. (1984) indicates that the greatest variability of petiole nitrate occurs in immature leaves in the upper portion of the plant.

The effect of plant density on N levels is not clear. Oosterhuis and Morris (1979) and Grimes et al. (1973) showed little effect from plant population, whereas work by Sunderman et al. (1979) showed a linear decrease in petiole NO_3 as the number of cotton rows per 102-cm bed increased from one to

four. Wanjura and Sunderman (1976) concluded that row spacing had little effect on plant N levels.

There are varietal differences in cotton N concentration (Oosterhuis & Morris, 1979; MacKenzie et al., 1963), but the effects of plant and soil factors are similar.

B. Phosphorus

1. Soil Factors

Phosphorus concentration in cotton plants may be increased by P fertilization (Cope, 1984; Khasawneh & Copeland, 1973; Sharpley & Reed, 1982; Stelley & Morris, 1953). In greenhouse sand culture trials, an increase in P in the solution had a direct effect on the level of P in the plants (Ergle & Eaton, 1957; Joham, 1951). However, other research has not been able to demonstrate this relationship (Clark, 1964; Janat & Stroehlein, 1986; Kapp et al., 1953).

Depth of P fertilizer placement did not have a consistent effect on P concentration (Kapp et al., 1953), and method of application (either drilled or broadcast) did not affect P concentrations (Stelley & Morris, 1953). Stelley and Morris (1953) found that liming acid soils had no effect on P concentration in cotton.

Maples et al. (1977) indicate that as petiole nitrate levels decline, petiole P concentrations increase if there is no water stress. However, in water-stressed plants, petiole P declines with petiole NO_3 . Sharpley and Reed (1982) found that in water-stressed cotton, the rate of leaf P decline was slower than in nonwatered-stressed plants.

Drip irrigation could be used to apply P fertilizer throughout the season. This is not common, and research by Janat and Stroehlein (1986) found that P concentration of petioles was not increased by P fertilization through the drip system. Further, they found that the amount of P uptake by furrow and drip-irrigated cotton plants was similar.

The response of P concentration in cotton in N fertilization has been inconsistent. This response has been found to decrease (Joham, 1951), increase (Zelinski, 1986), or not affect (Clark, 1964; Zelinski, 1986) P concentration. Joham (1951) also found that K fertilization decreased petiole P concentrations. The interaction between P and Zn fertilization is well known, and Janat and Stroehlein (1986) indicated a possible reduction in petiole P by Zn fertilization.

2. Plant Factors

A decrease in P concentration of cotton tissues throughout the season has been found and is considered normal (Bassett et al., 1970; Janat & Stroehlein, 1986; Sharpley & Reed, 1982); however, exceptions have been reported (Maples et al., 1977). In contrast to the usual decline, P level in seeds increased over time (Bassett et al., 1970). From the information provided by Bassett et al. (1970) and Kapp et al. (1953), cotton tissue can be listed in

order of increasing P concentration: roots, stems, mature leaves, immature leaves, fruiting parts, and finally seed.

Root growth and P uptake were found to be closely related (Khasawneh & Copeland, 1973). The amount of P taken up per unit length of root was the same regardless of P concentration in solution.

C. Potassium

1. Soil Factors

Soil K levels have been found to have a direct effect on K concentration in vegetative structures (Bennett et al., 1965; Cope, 1984). Fertilization with K has also been shown to increase K concentration in cotton (Fullmer & Stromberg, 1964; Hsu et al., 1978; Joham, 1951; Page et al., 1963). Cassmen et al. (1986) suggest that the level of NH_4OAc extractable K at the 20- to 40-cm depth is a more reliable predictor of available K than is extractable K in the 0- to 20-cm depth.

Method of fertilizer application was investigated by Fullmer and Stromberg (1964). On soils with low cation exchange capacity (CEC), broadcasting the fertilizer produced higher petiole K levels than did banding, but on soils with high CEC, drilling was more effective. Fertilizer application anytime before peak bloom was acceptable.

Substantial research has not been done on the effects of other fertilizer on K levels in cotton. Work by Zelinski (1986) showed no effect on petiole or blade K concentration as a result of N fertilization. Joham (1951) also found no effect from either N or P fertilization.

2. Plant Factors

Throughout the season, K concentration in cotton tissue declines in vegetative plant parts (Stromberg, 1960; Joham, 1951). Bassett et al. (1970) found that K concentration in cottonseed was constant, and Bennett et al. (1965) indicated that K concentration of reproductive structures (squares and bolls) did not change significantly throughout the season.

Differences in K concentration due to variety have been investigated (Weir et al., 1986; Page et al., 1963). There are few differences in either concentration or pattern throughout the season.

D. Secondary Nutrients

Research on secondary nutrients is considerably less than on N, P, and K. Therefore, our information is incomplete and many areas of potential research are available.

1. Calcium

Calcium availability in soils is most frequently related to the pH of the soil. If soil pH is low, there is a possibility of Ca deficiency. However, toxic

levels of Al, H, Mn, or Fe are more likely. There has been little research involved with Ca fertilization that was not directly related to soil pH modification, but we can conclude that most soil conditions do not limit the Ca uptake by cotton.

Fertilization with other nutrients may have an effect on the concentration of Ca in cotton leaf blades or petioles. Fullmer and Stromberg (1964) and Joham (1951) showed that K fertilization reduced the Ca level in cotton petioles. Joham (1951) indicated that fertilization with P increased Ca concentration. Zelinski (1986) found that N fertilization either decreased or had no effect on Ca concentration in cotton leaf blades collected at peak bloom.

McHargue (1926) analyzed mature cotton plants in Mississippi and found the following Ca concentrations (g kg^{-1}) leaves (44), stems (14), kernels (1.9), hulls (1.4), and fiber (1.3). Research by Fullmer and Stromberg (1964) found that Ca concentration remained fairly uniform throughout the season.

2. Magnesium

Magnesium deficiencies can occur in the southeastern USA (Gheesling & Perkins, 1970). The same authors, working with solution culture, indicated that increases in substrate Mg increase the Mg level in cotton blades, petioles, and stems. They also found that Mg concentration in leaf blades that were adequately supplied with Mg remained fairly constant throughout the experiment (i.e., at least 100 d after planting). The Mg concentration in petioles and stems varied to greater extent than in blades, and the authors indicated that the blade was probably the best tissue for determining deficiency. Fullmer and Stromberg (1964) found that Mg concentration in petioles increased throughout the season.

The effects of N, P, and K fertilization on the Mg levels in blades or petioles have been investigated. Zelinski (1986) found that N fertilization increased leaf blade Mg in one year but not in the next. Joham (1951) found that N fertilization increased Mg levels, that P had no effect on Mg levels, and that K fertilization decreased leaf Mg levels. Fullmer and Stromberg (1964) found that K fertilization decreased the Mg concentration of cotton petioles.

3. Sulfur

In soils, available S comes from the decomposition of organic matter, soluble sulfate, and from release of sulfates that have been adsorbed to the mineral fraction of the soil. Fertilization with S-containing materials has been shown to increase the levels of S in leaf blades (Barton et al., 1982) and in both leaf blades and petioles (Jordan, 1964). In a solution culture experiment, Gaines and Phatak (1982) showed that as the substrate level of S increased, there was an increase in total plant S.

Research by McHargue (1926) found the following S concentration (g kg^{-1}): leaves (22), stems (4.3), kernels (3.6), and hulls (0.38).

The effect of other fertilizer nutrient additions on the S concentration has not been widely studied. Zelinski (1986) found that N fertilization slightly

lowered the sulfate-S levels in leaf blades in one year but had no effect in the other year of the study.

E. Micronutrients

Field research on micronutrient concentration in cotton tissue is difficult due to soil variability, and much of the information has been developed using solution culture. Therefore, much of the interpretation relies on extrapolation of field conditions.

Increases in substrate level generally increased the levels of nutrients in cotton tissue. This increase was demonstrated for Zn by El-Gharably and Knezek (1980), Joham and Rowe (1975), Ohki (1975b) and Rehab and Wallace (1978), for Mn by Foy et al. (1969), Gheesling and Perkins (1970), and Ohki (1974), for B by Ohki (1974) and Oertli and Roth (1969), and for Mo by Amin and Joham (1960). Other research by Amin and Joham (1958) found a good correlation between water extractable Mo in soils and tissue concentration of Mo. Foy et al. (1969) also found in soils that NH_4OAc -extractable Mn was not related to plant Mn concentration.

The effect of liming on the concentration of nutrients in cotton tissues indicated that liming a soil from pH 4.4 to 7.3 decreased the Mn concentration but had no effect on Fe concentration (Hati et al., 1979). Scott et al. (1975) found that liming reduced that B concentration in cotton 30- to 65-d old.

The effect of other nutrients has received little study, but a few relationships have been found. Ohki (1974) found that high levels of B slightly increased the Mn concentration, but that B level had little effect on the concentrations of Zn, Cu, or Fe (Ohki, 1975a). Rehab and Wallace (1978) found no effect on Zn levels by increasing substrate levels of Cu and Mn, but that higher levels of Co decreased Zn concentration.

Unlike the macronutrients, the concentration of micronutrients can remain fairly constant throughout the season. Joham and Rowe (1975) found that Zn concentration in cotton leaf tissue was 75, 84, and 68 mg kg^{-1} at 54, 72, and 130 d after planting, respectively. Gheesling and Perkins (1970) found that Mn concentration in leaves remained between 70 and 90 mg kg^{-1} for the first 120 d after planting. Total plant B concentration also remained stable (i.e., 9–12 mg kg^{-1}) in cotton 30- to 65-d old (Scott et al., 1975).

Different varieties have not been shown to affect the concentration of nutrients. This was shown to be the case for Zn by Rehab and Wallace (1978), for Mn by Foy et al. (1969), and for Mo and Mn by Bhatt and Appukuttan (1982).

III. USE AND INTERPRETATION OF COTTON TISSUE ANALYSIS

A. Introduction

The interpretation of nutrient uptake and foliar analysis has been approached differently in the humid and semiarid regions of the USA. Leaf blades are taken for analysis in the humid region while petioles are taken

in the semiarid area. The less-determinate varieties grown in desert areas lend themselves to diagnosis and treatment during the growing season. On the other hand, most nutritional problems diagnosed in more determinate cotton varieties of the Southeast cannot usually be corrected during the same growing season due to their short effective bloom and boll-setting period. A prognosis for seasonal correction of soil fertility difficulties is often possible with irrigated cotton in arid regions because of either a longer bloom period or, in some areas, two distinct bloom periods. Because of the predictable desert environment, determination of transitory nutrients (as found in the petiole) has proven successful. However, petiole sampling programs have been adapted to some humid areas in Arkansas and Georgia (W.E. Sabbe, 1985, personal communication). The leaf blade has been selected for analysis where the seasonal and daily climate has proved to be less predictable. Weather fluctuations affect nutrient content of leaf blades less than nutrient content of petioles. Because of the differences in culture, variety, and plant part between the cotton-growing areas, the discussion on plant analysis has been divided into petiole and leaf blade analysis.

B. Diagnosis

1. Leaf Blade Analysis

Perhaps the greatest use of leaf blade analysis is to judge the efficiency of a fertilizer practice, since leaves are accumulators of nutrients and tend to be less affected by climate and seasonal changes than petioles. The more stable nutrient concentration enables the producer to sample his crop in a more relaxed manner than would be possible with petioles because of the less rapid changes in concentration of nutrients in the leaf blades.

Concentration of nutrients in leaf blades is affected by sampling dates or stage of growth. Whole plant analyses show that early uptake of nutrients is greater in proportion to the dry weight produced (Table 18-2). The top leaf and top petiole differ in their accumulation of Ca and Mg. Whereas the level of these two nutrients decreased in the petioles with time, it increased in the leaves. A smaller reduction occurred with time in the boll compared with other plant parts. Bolls are becoming larger in the intervals between sampling, and the accumulation of K during this period resulted in lower concentration elsewhere in the plant. Potassium fertilizer increased the level of K in all plant parts, and the magnitude of the increase at the various sampling dates was dependent upon the fertilizer rate (Table 18-5).

It can be speculated that nutrient concentration ratios of top to bottom leaves may be better indicators of plant nutrient status than concentration in a single leaf from either position. Such ratios should be closer to unity in normal plants than in those with a deficiency, since translocation of nutrients to points of active growth in deficient plants is expected to result in wider ratios (Sabbe, 1974).

Analysis of cotton leaves collected by surveys in Arkansas and Georgia and from research plots in Alabama indicated fair agreement for most

Table 18-5. Effect of K fertilizer levels on K changes in plant parts (Sabbe & MacKenzie, 1973).

Plant part	Date	kg K ha ⁻¹					
		0	69	138	276	414	552
		g K kg ⁻¹					
New growth and leaves	24 July	16.2	19.4	22.0	24.7	28.5	28.3
	22 Aug.	8.5	11.5	16.9	21.2	21.1	24.7
Top mature leaves	24 July	10.1	14.8	19.4	25.8	27.6	31.4
	22 Aug.	6.6	9.9	14.4	16.0	20.7	29.0
Old leaves plus petioles	24 July	11.3	23.0	32.3	41.9	41.8	47.0
	22 Aug.	7.7	13.9	15.8	31.9	35.0	40.9
Stems	24 July	12.4	19.4	26.2	30.4	32.8	34.9
	22 Aug.	3.7	8.3	12.1	16.5	20.0	17.2
Bolls	24 July	18.8	21.2	23.2	24.3	25.9	25.2
	22 Aug.	15.0	17.5	19.2	22.0	22.0	22.5
Percentage decrease (avg.) between 24 July and 22 Aug.		40	38	36	27	24	19

nutrients (Table 18-6). However, Cope (1984) indicated that sampling over several years may be necessary to determine the variation among locations and years. Therefore, the paired plot technique (good and bad areas within a field) may improve the diagnosis of a plant analysis.

Sufficiency ranges for cotton nutrients in Arkansas and Georgia are given in Table 18-7. In spite of differences in time and methods of sampling, the two values are quite similar. Sabbe et al. (1972) reported that differences occurred in leaf Fe and Mn concentrations between cotton grown on alluvial soil and that grown on loessial soil. Other nutrient concentrations were similar between the two soil groups in Arkansas.

Kallinis and Kouskoleka (1967) reported that the Mo concentration in mature leaves of cotton grown in nutrient culture needs to be above 1.9 mg kg⁻¹. Leaves at this level showed incipient deficiency symptoms whereas leaves containing 2.4 mg kg⁻¹ were healthy. Kouskoleka and Kallinis (1968)

Table 18-6. Nutrient concentrations of cotton leaves within the humid cotton growing region.

Date	Samples	N	P	K	Ca	Mg	Mn	Fe	B	Cu	Zn
<div><div>g kg⁻¹</div><div>mg kg⁻¹</div></div>											
Arkansas (Sabbe et al., 1972)											
23 July 1968	384	40.1	5.0	13.7	25.3	5.5	74	88			56
5 Aug. 1970	259	33.3	5.0	15.8	28.4	7.2	180	177			61
12 Aug. 1969	223	30.2	3.7	13.8	29.9	7.1	126	151			46
Georgia (Anderson et al., 1971)											
June-July 1971	284	41.8	3.3	20.9	25.6	5.2	225	139	27	9	24
Alabama (Cope, 1984)											
Early bloom 1971	384	44.4	3.7	14.0	21.7	8.1	160	71	40		24

Table 18-7. Selected state sufficiency ranges for nutrients in cotton leaves.

Nutrient	Arkansas†	Georgia‡
	<hr/> g kg ⁻¹ <hr/>	
N	30.0-43.0	35.0-45.0
P	3.0-6.4	3.0-5.0
K	9.0-19.5	15.0-30.0
Ca	19.0-35.0	20.0-30.0
Mg	3.0-7.5	3.0-9.0
S	3.0-7.5§	2.5-8.0
	<hr/> mg kg ⁻¹ <hr/>	
Mn	30-300	25-350
Fe	30-300	50-250
B	20+	20-60
Cu	NA¶	5-25
Zn	20-100	20-200

† Sabbe and MacKenzie (1973.)

§ W.E. Sabbe (1985, unpublished data).

‡ Plank (1979).

¶ NA = Not available.

found the critical Fe concentration to be 85 to 112 and 57 to 88 mg kg⁻¹ in young and mature cotton blades, respectively. These values were obtained in solution culture and are considerably higher than the lower end of the sufficiency ranges for this nutrient in Georgia (50 mg kg⁻¹) and Arkansas (30 mg kg⁻¹). Another possible explanation of this lack of agreement is a differential variety response to substrate Fe concentration similar to that demonstrated for Mn. Foy et al. (1969) concluded that cotton varieties selected from a high-Mn soil exhibit a greater tolerance for Mn than cotton developed on a low-Mn soil. For example, a cotton variety in Arkansas showed an 8% decline in yield when 3700 mg kg⁻¹ of Mn was present in leaves, whereas the yield of a western cotton was reduced 13% when the leaves contained a somewhat lower level of 2456 mg kg⁻¹. At 100% relative yield, the Mn concentrations were 243 and 162 mg kg⁻¹ for the Arkansas and western varieties, respectively. In nutrient culture, Gheesling and Perkins (1970) found leaf blades to be the best indicator of the Mn status. Manganese deficiency was evident when the level was < 15 mg kg⁻¹. Joham and Amin (1967) classified cotton as a highly tolerant species based on its tissue Mn level.

The critical B concentration in young cotton leaves was about 15 mg kg⁻¹, whereas it was 5 to 10 mg kg⁻¹ higher in mature leaves (Murphy & Lancaster, 1971). Miley et al. (1969) found that B-deficiency symptoms occurred in later growth stages when the concentration was 18 mg kg⁻¹ in petioles sampled at the early bloom and early boll stages and 13 mg kg⁻¹ in leaf blades at early boll stage. Work in Zambia (Rothwell et al., 1967) indicates a leaf blade concentration of 28 mg kg⁻¹ B to be sufficient and a 5 mg kg⁻¹ B level to be deficient. Maximum growth was obtained in a nutrient culture containing 10 mg kg⁻¹ B, whereas a 30 and 40 mg kg⁻¹ B solution concentration reduced the growth to 40 and 10% of the maximum, respectively (Oertli & Roth, 1969). The B concentrations (plant tops) were approximately 160, 250, and 420 mg kg⁻¹, respectively. Ohki (1974) found that low concentration of substrate B increased the critical level of Mn in older leaf blades.

According to Elliot et al. (1968) problems with secondary and micronutrient deficiencies or toxicities are not common in cotton production. Studies in Georgia (Anderson & Harrison, 1970) show that plant tissue micronutrient (Mn, Fe, Zn, B, Cu, and Mo) concentration variations occurred among cotton varieties at each of three soil series locations as well as among locations. No correlation was found among total soil Mn, total soil Fe, or soil pH and Fe and Mn tissue levels.

Jordan (1964) increased the S concentration in cotton leaves and petioles by S fertilization. He concluded that a S concentration $< 2 \text{ g of S kg}^{-1}$ in either the leaf and petioles at midseason was deficient. In Arkansas, increases in leaf blade S were obtained with S fertilizer (Maples & Keogh, 1974). However, no yield increases were obtained when leaves contained at least 4 g of S kg^{-1} in this 3-yr study. Gheesling and Perkins (1970) stated that below 2 g of S kg^{-1} in the leaf blades deficiency symptoms would occur.

2. Petiole Analysis

Plant nutrient concentrations considered sufficient for optimum production at various cotton growth stages have been reported. Determination of P and K tissue levels appears to be most helpful for predicting the status of these nutrients in the following cotton crop (Fullmer & Stromberg, 1964). However, N analysis of cotton petioles does offer the most promise by forewarning the grower of imminent N deficiencies or surpluses. Both of these conditions can be determined early in the season and prevented, usually by adjustment of the current N fertilizer program. This approach has been used in the southwestern irrigated desert area where a long seasonal growth period allows the practice to be effective. A late-season petiole analysis can also be used to evaluate the current fertilization program and aid in plans for the next year.

a. Nitrogen. The pattern of seasonal $\text{NO}_3\text{-N}$ level in petioles in Arkansas is shown in Fig. 18-3. For optimum production, there is a characteristic level of $\text{NO}_3\text{-N}$ in cotton petioles of each variety and at each location. Nitrogen fertilization programs can be adjusted to maintain the recommended $\text{NO}_3\text{-N}$ concentration.

Joham (1951) recognized that petioles containing $< 55 \text{ mg of NO}_3\text{-N kg}^{-1}$ were associated with lower cotton yields in Texas. MacKenzie et al. (1963) defined the needed $\text{NO}_3\text{-N}$ concentrations in petioles as 16 000, 8000, and 2000 mg kg^{-1} for plants in early, mid-, and late-blossom stage of growth, respectively, for the lower desert areas of California. In Arizona, Tucker (1963) recommended levels of 15 000, 12 000, 6 to 8000, and 4000 $\text{mg of NO}_3\text{-N kg}^{-1}$ for the respective growth stages of first square, first flower, first boll, and first open boll.

Under Arkansas growing conditions, the sufficiency range for petiole $\text{NO}_3\text{-N}$ was 12 to 28, 8 to 24, 4 to 15, and 2 to 6 g kg^{-1} for 1 July, 15 July, 1 August, and 15 August, respectively (Maples et al., 1977). These authors and Amer and Abuamin (1969) suggested that the petiole level as a criterion

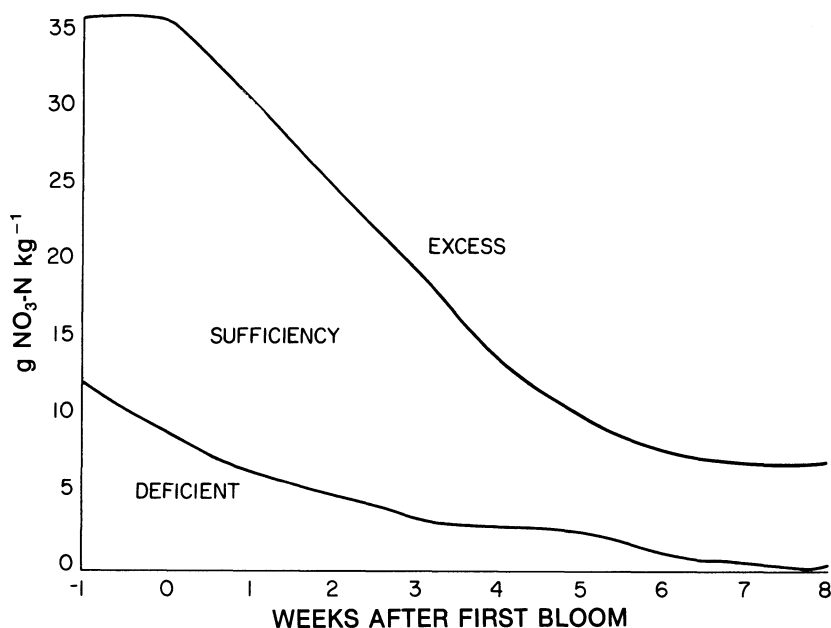


Fig. 18-3. Sufficiency range for cotton petiole NO_3 in Arkansas (Maples et al., 1977).

for plant N status was useful only if the crop was not affected by uncontrollable factors such as salinity, drought, insect, and diseases.

Regardless of whether petioles are used for diagnostic or monitoring purposes, sampling variability has to be considered (Tabor et al., 1984). In commercial, irrigated fields, petioles from the first mature leaf were best, but if the maturity of the leaf is in question, the petiole from the next older leaf should be taken.

Grimes et al. (1973) designed a model for estimating the desired $\text{NO}_3\text{-N}$ levels in cotton petioles using N fertilization, time of season, and water management. Other authors reported that petiole NO_3 differ among cultivars, rowing spacings, and N application rate (Sunderman et al., 1979); however, no differences were found when foliar N was applied (Jenkins et al., 1982). Barton et al. (1982) reported that the concentration of plant S affected both the leaf N and petiole NO_3 levels. Therefore, knowledge of the plant S status is necessary prior to interpretation of petiole NO_3 for cotton N status.

b. Phosphorus. Concentration of P in cotton has not been studied as completely as that of N and K because many of the cotton soils contain ample available P. Consequently, fertilization with this nutrient has not always raised yields. Nevertheless, nutrient status levels have been established for P (Jones & Bardsley, 1968). In the southwestern USA desert area, petioles will contain, throughout the season, at least 0.15% P on a dry weight basis. A level of 1000 mg kg^{-1} petiole P until after peak bloom is recommended as a sufficiency level by Basset and Mikkelsen (1962). Joham (1951) suggested

0.16% P on a fresh petiole weight basis as the critical level needed for a 90-d-old, field-grown plant. Using field test methods, Wickstrom et al. (1964) suggested that, for maximum production, P levels should be high during early bloom and boll development, whereas medium levels are satisfactory during the late growth periods. They also suggested using the petiole of the basal leaf until early bloom and the petiole of the first mature leaf after bloom.

c. Potassium. Joham (1951) has reported the K concentration in dried petioles of high-yielding greenhouse cotton plants at 60, 90, and 145 d after emergence to be 6.0, 4.1, and 3.0%, respectively. In Brazil, de Mello et al. (1960a, b) found that, during the early bloom stage (90 d after planting), K levels of 1.8% in petioles were necessary for maximum production. In California, Fullmer and Stromberg (1964) concluded that petioles should contain at least 4.5% K at early bloom and 1% K at 130 d after planting. Using field test techniques, Wickstrom et al. (1964) recommended high K levels in petioles during the early bloom and boll development periods; however, a medium level was adequate for later growth periods.

C. Monitoring Nutrient Uptake

Enough information is available in certain cotton-producing areas for the interpretation of cotton plant analysis. Nutrient levels corresponding to deficiency and optimum growth conditions have been established for the most common limiting nutrients (N, P, and K). However, interpretation of plant analysis results is not entirely straightforward because of interactions among these and other nutrients (Belousov & Sdizhenskaja, 1954; Dastur, 1959; Hardy, 1962; Joham, 1951).

Characteristically, the N, P, and K levels in cotton petioles or blades will be high during the early stages of growth and then decrease during fruiting and maturation (Fullmer & Stromberg, 1964; Joham, 1951; MacKenzie et al., 1963). For this reason, plant analysis levels for various growth stages, such as early, mid-, and late-bloom, are important because they will indicate whether the crop has sufficient nutrients for continued optimum production. Since cotton production involves the growth of many varieties in different soil, climatic, and management environments, it is unreasonable to expect sufficiency levels for one cotton-growing area to be applicable to another region. Differences in the nutrient sufficiency levels necessary for optimum cotton yields are determined mainly by local conditions; they must, therefore, be measured locally.

Plant analysis has been used by cotton growers in the desert areas of the southwestern states of the USA to assist in controlling the N, nutrition of their crops. The soils of the area are typically low in N and cotton production, therefore, depends upon fertilizer N. Petiole analysis indicates N needs approximately 2 wk before visual deficiencies appeared (Gardener & Tucker, 1967). Depletion of N at the end of the season is desirable for easier defoliation and harvesting. Two petiole samples are recommended as a guide for N application, the first at early fruiting stage, and the second at early flower stage.

The use of petiole NO_3 to ascertain the N nutritional status of the cotton plant has been successful in irrigated fields in semiarid regions where soil N is a limiting factor, but it has not proven as successful in humid areas. Maples et al. (1977) developed a petiole monitoring program that has been used in Arkansas since 1977. This program is based not only on the petiole analysis for NO_3 but also on the petiole analysis for P, knowledge of the plants fruiting status, the soil moisture level, and previous N fertilization. Maples and Miley (1978) described the program as a N management system in which the N inputs are regulated throughout the season (10 weekly petiole samples starting 1 wk before fruit bloom) and the goal is to maximize yields in favorable growing seasons and minimize problems in unfavorable seasons.

Researchers in other states or countries have not been as enthusiastic regarding petiole nitrates as an indicator of plant N status. In research studies where no yield response was obtained with fertilizer N (Oosterhuis & Morris, 1979), where yields were also effected by rainfall (Touchton et al., 1981), or where yield did not correlate with petiole NO_3 (Koli & Morrill, 1976) a plant NO_3 monitoring program was not recommended. Additionally, Oosterhuis and Bate (1983) suggested that the NO_3 reductase activity may be a convenient, reliable, and sensitive indicator of plant N status. Researchers in Mississippi reported that while no consistent relationship existed between petiole NO_3 and maximum yield, the petiole NO_3 could be used to identify N deficiency/excess during the fruiting period (Thom & Spurgeon, 1982). The recommended rate ($100\text{--}115 \text{ kg of N ha}^{-1}$) did produce optimum petiole NO_3 concentrations under the environmental and soil conditions of the study. For cotton grown under irrigation on the Texas high plains, Sunderman et al. (1979) concluded that within the same year and within a location that the petiole N level could be an indicator of both the N fertilizer rate and the N status of the plant.

Growers interested in their fertilizer programs are starting plant analysis operations of their own or are subscribing to the services of commercial laboratories (Tabor et al., 1984). Phosphorus analysis may be included. Some fertilizer dealers also are offering plant analysis as a part of their service to customers. Either field tests or laboratory analysis may be offered in these cases depending upon the individual dealer involved. A big factor in the success of these commercial plant analysis operations is the turn-around service. This allows the grower to immediately evaluate the fertility status or trend of his crop and to make adjustments when necessary to ensure a well but efficiently fertilized crop.

D. Fertilizer Recommendations

The response of cotton to fertilizer follows that of a nonleguminous crop (i.e., the amount of N sets the level of yield). Engelstad and Terman (1966) reported that significant cotton yield responses in Mississippi to N, P, and K fertilization occurred at an application frequency of 70, 5, and 20%, respectively. The University of Arkansas Soil Testing Program recommended N, P, and K fertilizer on 98, 45, and 67%, respectively, of the 46 000 soil sam-

ples from cotton fields submitted for fertilizer recommendations during 1980 to 1984 (W.E. Sabbe, 1985, unpublished data). Maples and Frizzell (1985) concluded that the yield potential for different cotton cultivars was a valid parameter for modifying general fertilizer N recommendations. Additionally, excessive N rates increased the management needed to avoid yield losses, and that made yield losses on non-uniform fields unavoidable because of the varying management practices needed for each soil type (Maples et al., 1987).

Since N is related directly to yield potential, the irrigated desert USA areas require about 150 kg of N ha⁻¹, the rainfed humid southeast USA requires about 100 kg of N ha⁻¹, and the upland plain areas of Texas require about 50 kg of N ha⁻¹ (Tucker & Tucker, 1968). As management practices improve and as higher yields are required, the application rate will continue to increase. However, Maples and Keogh (1971) concluded that when excess N was applied in the humid areas, not only was maturity delayed but the residual N affected yields in subsequent years.

The fertilizer rate for P and K fertilizer is determined not only by crop response but also by soil characteristics. The availability of P and K during a growing season can be estimated via a soil test method adapted for that particular soil physiographic area (Jones, 1980).

Annual P fertilizer applications up to 55 kg of P ha⁻¹ are required in the southeast USA where the soils have the capacity of "fix" P. The yields in the irrigated southwest area have recommendations up to 40 kg of P ha⁻¹ (Jones & Bardsley, 1968). Cope (1984) reported that a soil test for P gave a good measure of soil-available P and was correlated with the fertilizer-applied P.

The recommended rate of K fertilizer varies up to 330 kg of K ha⁻¹, the actual rate depends mainly on soil characteristics such as fixation and texture (Kamprath & Welch, 1968). A residual K study indicated a significant correlation among K fertilizer rates, soil test K, and leaf K and yield with the best response closely related to the soil test K (Cope, 1984). A characteristic of the yield response to fertilizer K is a response only to the first increment of fertilizer K (Lombin & Mustafa, 1981). However, a positive correlation between fertilizer K and petiole K concentration was observed in California (L.J. Zelinski, 1986, personal communication). With the exception of the Atlantic Coastal Plains, S deficiencies usually are not present. In that soil region, an application of about 20 to 30 kg of S ha⁻¹ is recommended for a two bale crop (Standford & Jordan, 1966). Barton et al. (1982) reported that the concentration of plant S affected both the leaf N and petiole NO₃ levels. Therefore, knowledge of the plant S status is necessary prior to interpretation of petiole NO₃ for cotton N status. Miley et al. (1969) and Maples and Keogh (1974) obtained very few responses to S fertilization on alluvial soils in Arkansas.

A characteristic of yield responses to fertilizer applications was reported by Cope (1984) on two fertility studies that encompassed an 18- or 24-yr period, respectively. The 67 kg of N ha⁻¹ application produced more than

90% of the top yield, whereas a soil test proved to be a reliable indicator of the P and K fertilizer needs.

The deficiency symptoms of other secondary and micronutrients are known (Marcus-Wyner & Rains, 1982); however, most production cotton fields appear to have adequate levels for optimum yields (Hinkle & Brown, 1968).

In summary, plant analysis monitoring programs have been established in both cotton-growing areas of the USA. The greatest success appears to be where some of the environmental conditions are predictable/controlled and where N management is a season-long consideration.

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Chapter 19

Plant Analysis as an Aid in Fertilizing Small Grains

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Production constraints on producers and public concern over the environmental impact of fertilizer use emphasize the need for efficient fertilization programs. Proper fertilizer application ensures efficient plant use and minimum movement into non-target areas. Time and method of fertilizer application can greatly influence plant utilization and fate of fertilizers in the environment. In current agricultural production systems, we must integrate the public concerns over the environment, as affected by agriculture, and the producer's concern for achieving optimum economic return for his fertilizer investment. Soil testing is one diagnostic tool that has been used successfully for many years to improve fertilizer efficiency and economic return in small grains. More recently, plant analysis has been used as another tool to complement soil testing in developing efficient small-grain fertilization programs. Its use, in conjunction with soil testing, can greatly improve fertilizer efficiency and minimize losses into the environment when tempered with observation and experience. Small-grain production and quality are greatly influenced by fertilization. Proper fertility favors high yields of quality grain. The objective of this chapter is to provide the scientific basis for small-grain plant analysis and its use to assess the nutrient status and fertilizer requirements of these crops. The small grains discussed are wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), oat (*Avena sativa* L.), and rice (*Oryza sativa* L.).

I. PREVIOUS USE OF PLANT ANALYSIS

An interest in the chemical composition of small grains was reported as early as 1939 by Miller who collected plant samples from winter wheat fields. Over a 4-yr sampling period, he found large decreases in N and K concentrations as the plants approached maturity. The change in P concentration was much less. The largest changes occurred from Feekes stage 3 to 10 (tillering to boot; Large, 1954). The Feekes scale will be used throughout the remainder of this chapter and will be referred to as stages of growth from 1 to 11.4 (emerging to maturity).

Extensive work on the nutrient concentration of wheat at various locations was reported by Johnson and Schrenk (1953). Plant samples collected from various locations over a 14-yr period showed an average composition of whole plants at tillering (stage 2) as follows: 47.2 g kg⁻¹ of N; 2.2 g kg⁻¹ of P; 32 g kg⁻¹ of K; 3.6 g kg⁻¹ of Ca; 1.2 g kg⁻¹ of Mg; 92 mg kg⁻¹ of Mn; 208 mg kg⁻¹ of Fe; and 20 mg kg⁻¹ of Cu. Variation in nutrient concentrations with time was also clearly shown, with N, K, Ca, and Mg decreasing the most as plants approached maturity.

A review of the effect of soil types and fertilizers on the chemical composition of small grains (Vandecaveye, 1940) reported that the nature and quantity of available nutrients in the soil greatly influenced the concentration in the plant. Past cropping sequence, soil texture, organic matter, pH, and parent material were factors that influenced nutrient availability to the greatest extent. Nitrogen fertilizer increased N concentration in wheat plants sampled at various growth stages. At maturity, however, protein concentration of the grain was not always increased by N fertilizer. Nitrogen fertilizer was reported to decrease P and Ca concentrations and to occasionally increase N concentration in oat sampled at the hay stage (stages 10.1–10.2).

Johnson and Schrenk (1953) reported that fertilizer application had a direct influence on the nutrient concentration of wheat. Plants receiving no P fertilizer contained 1.9 g kg⁻¹ of P at tillering (stage 3) compared to 2.6 g kg⁻¹ P for those receiving P. Plant samples collected during the second year of study showed the residual effect of fertilization on nutrient concentration.

Greaves et al. (1940) found large variations in nutrient concentrations between varieties and years in spring and winter wheat varieties. Green manure treatments had limited influence on nutrient concentrations. Spring wheat varieties were found to contain slightly higher nutrient concentrations than winter wheat varieties. More recently, Ward et al. (1973) summarized the influence of various factors on nutrient concentration in plants and suggested uses and interpretation of plant analysis in maximizing economic return for fertilizer use.

Early studies on the use of plant analysis for rice were conducted in Asian countries. The need for proper management of N was recognized and initial work involved this problem. An asparagine test to determine mid-season needs for supplemental N was developed by Ozaki (1955). Absence of asparagine in the youngest leaf at 3 to 4 wk before heading indicated a need for addi-

tional N. The asparagine test was reported to be effective for determining the need for mid-season N, but the appearance of asparagine in the plant was influenced by light (Mitsui et al., 1959) and NH_4 (Sing et al., 1960). Early studies to correlate total N in the leaves to N fertilizer needs yielded variable results. Maume and Dulac (1954) concluded that a high level of N in rice leaves was essential for high yields, but the correlation between N concentration and yield was not very good. They also found that the highest concentrations of P and K were associated with high rice yields, but again, the relationships observed between yields and P and K concentrations in the leaf were not good.

There have been numerous other reports on plant analysis of rice in the world. Tanaka and Yoshida (1970) found that the critical level of N in the leaf blade at the tillering stage was 26 g kg^{-1} of N. Lian (1972) used plant analysis to determine the N requirement of Asian rice with some success. Phosphorus deficiency in rice was diagnosed in Taiwan by investigating P distribution changes in various plant parts at different growth stages (Houng et al., 1971). Ishizuka and Tanaka (1951) showed that K deficiency existed in rice straw when its K_2O concentration was $< 10 \text{ g kg}^{-1}$. Kiuchi and Ishizuka (1961) found that the straw content of 20 g kg^{-1} of K was required for high rice yield. The critical K concentration in the leaf blade was shown to be 10 g kg^{-1} at tillering and harvest by Tanaka and Yoshida (1970). Studies in Taiwan, by Sheng et al. (1964), indicated that a K concentration of 17 to 18 g kg^{-1} was necessary for near-maximum rice yield. Su (1976) found that the critical concentration of K in the straw depended on N and P status of the soils in the Philippines and Indonesia. Wallihan and Sharpless (1974) found that the N/S ratio and the S content were both useful indicators of the S status of the rice plant. Wang (1976) reported the critical S concentration in rice straw grown in the Amazon basin of Brazil was 0.5 g kg^{-1} at harvest. Other investigators have found plant analysis to be valuable in assessing the Zn (Mikkelsen & Brandon, 1975; Forno et al., 1975; Sedberry et al., 1980) and Si status (Lian, 1976) of rice.

Rice plant analysis studies were initiated in the 1960s in the USA. Thenabadu (1966) published the first tentative critical N concentration values for rice. Shortly after this, Mikkelsen et al. (1970) reported tentative critical concentrations of N, P, and K in California. Critical N, P, and K concentrations developed by Mikkelsen and Hunziker (1971) were used as a guide in surveying the nutritional status of 325 California rice fields. The critical N concentration in the "Y" leaf (most recently mature leaf) at panicle initiation used in their studies was 24 to 26 g kg^{-1} of total N. The critical concentrations of P and K were 0.6 to 0.8 g kg^{-1} of $\text{PO}_4\text{-P}$ and 6 to 7 g kg^{-1} of K, respectively. However, the critical nutrient levels developed in California were not applicable to cultivars grown in the south-central USA because of cultivar, cultural system, and climatic differences (Ward et al., 1973). Normal N concentrations in the most recent fully expanded leaf of eight rice cultivars grown in Texas varied with cultivar and time of sampling.

More recent research shows that rice plant analysis is a valuable diagnostic aid in determining the nutritional status and fertilizer requirements of

rice. Brandon et al. (1980) and Mikkelsen (1983) reported both the critical concentrations and adequate ranges of N, $\text{PO}_4\text{-P}$, and K for semidwarf rice cultivars currently grown in California. Critical concentrations and adequate ranges were reported by growth stage because concentrations of these plant nutrients change with sequential stages of plant development. The Y leaf should be collected at the mid-tillering, maximum tillering, and panicle initiation stages to monitor concentration changes over time. Multiple sampling times improved the precision of estimating N, P, and K fertilizer requirements. Plant analysis is currently used in California to refine rice fertilization practices because of beneficial effects on pest management (Flint, 1983) and fertilizer efficiency. Critical N concentrations have been developed specifically for major commercial rice cultivars widely grown in California (Brandon et al., 1981a).

The relationship between Y leaf N concentration and grain yield of rice cultivars grown in the southern USA has been reported by Brandon and Wells (1986), Brandon et al. (1981a), and Brandon et al. (1982). Their studies showed progressively greater N concentrations in the rice plant with incremental increases of N fertilizer and a close relationship between Y leaf N concentration at different plant growth stages and grain yield. The critical N concentration range was identified at 25 to 32 g kg⁻¹ of total N, depending on rice cultivar and plant growth stage (Brandon & Wells, 1986). Long-grain, semidwarf Indica rices usually required higher plant N concentrations than long- and medium-grain tall rice varieties for maximum grain yield. Field studies confirmed the efficacy of plant analysis for N in both dry- and water-seeded cultural systems used in Louisiana (Helms, 1984). Considerable research has been conducted on the use of plant analysis in small grains. The vast majority of this research simply relates plant nutrient levels to soil nutrient availability (fertility level) and plant development. Few researchers have attempted to establish critical nutrient levels or to field-verify critical nutrient levels over different soils, environments, and years. Additional work in this area is needed. The next section summarizes factors that influence nutrient concentrations in the plant. When one reviews the literature in this area, an appreciation is gained of the problems and challenges encountered in establishing critical nutrient levels.

II. FACTORS INFLUENCING THE CONCENTRATION OF PLANT NUTRIENTS

Nutrient concentrations in plants are greatly influenced by soil and plant factors and their interactions with environmental conditions. An understanding of these environmental influences is necessary to improve the predictive precision of plant analysis as an aid in fertilizing small grains.

A. Soil Factors

Nutrient assimilation by plants is primarily through the root system. Root surface area, soil nutrient availability, and the soil environment for root

growth have a major impact on nutrient assimilation. Among the soil factors are fertility status, temperature, and moisture.

1. Soil Fertility

Numerous investigators have found that small grains respond to fertilizer when the native soil nutrient availability is low or adverse environmental conditions occur. Where grain yields have been increased by fertilization, an increase in the plant nutrient concentration has been frequently found if samples were collected before heading (stage 10.3). Working with rice, Sims and Blackmon (1967) and Lin et al. (1973) found that the $\text{NH}_4\text{-N}$ concentration in soils after 6 d of incubation under anaerobic conditions was highly correlated with N uptake and content. Bajaj et al. (1967) found that available soil N, based on an alkaline permanganate test method, was generally correlated with N uptake by rice.

Several studies have also shown that timing and method of N and P application influence the plant nutrient content. Phosphorus placed near the wheat seed as a starter, or in a concentrated zone, gives higher plant P concentrations than broadcast P applications (Peterson et al., 1981; Westerman & Edlund, 1985; Leikam et al., 1983; Maxwell et al., 1984; Westfall et al., 1987). Relatively late applications of $\text{SO}_4\text{-S}$ have proven to be effective in increasing yield of soft red winter wheat and yield and S concentration in the upper two leaves at Feekes stage 7 in Arkansas (Wells et al., 1986). Brandon et al. (1982) reported that the time of N fertilizer application in relation to permanently flooding the soil under rice production greatly influenced its N content. Proper timing of N fertilizer and water management were necessary to conserve N in the flooded soil system and positively influence N uptake by the plant. The concentrations of P (Houng et al., 1971) and K (Tanaka & Yoshida, 1970) in rice are directly influenced by soil nutrient content. The relationship between soil Zn level and Zn concentration in rice has been widely studied. Tanaka and Yoshida (1970) and Mikkelsen and Brandon (1975) showed a close relationship between available Zn and Zn concentration in rice seedlings. Studies by other investigators (Sedberry et al., 1971; Mikkelsen & Kuo, 1977) confirmed that increased soil Zn availability increased the Zn concentration in rice.

The application of one nutrient has also been found to influence the plant concentration of other nutrients. Singh et al. (1986) found that P fertilization increased soil P levels and tissue P concentration of spring wheat at Feekes stages 6 and 10, but resulted in a significant decrease in tissue Zn concentration. Westfall et al. (1973) found that the concentrations of Mg, Mn, Fe, and Ca were lower in N-deficient than in N-sufficient rice plants. The concentration of Zn in the rice plant depends on the soil factors of pH, oxidation-reduction potential, organic matter, and the soil concentrations of HCO_3 , P, and organic acids (Mikkelsen & Kuo, 1977; Yoshida & Tanaka, 1969). Nielson et al. (1960) reported that the application of K increased the K concentration of oat plants at the 7-leaf (Feekes 3) and heading (Feekes 10.3–10.5) stages, but depressed Mg and Ca concentrations, especially Mg,

while having little effect on N and P. The critical concentration of K in rice depends on the N and P status of the soil (Su, 1976). Su (1976) showed that K in rice straw was rather constant under low soil N and P conditions and that plant analysis for K was valid only when adequate N and P were available in the soil.

Vandecaveye (1940) reported that past cropping sequences and several soil properties such as texture, organic matter, pH, and parent material also influence nutrient availability. Crooke and Knight (1971) used a granitic soil limed in increments from pH 4.5 to 7.5 to determine the variation in nutrient composition of oat, barley, and winter wheat. Liming produced an increase in N and P concentrations in the three cereals to a soil pH of 6.5 or greater. Sulfur and Fe concentrations changed little with liming, while Ca, Mg, and K increased. Manganese concentration was reduced with liming, leveling off at about 30 mg kg⁻¹ of Mg. Additional nutrient interactional effect data could be cited; these examples illustrate the interactional effects that can occur.

2. Soil Temperature

Soil temperature has a large effect on plant growth through its effect on root growth and respiration. The N, P, K, and Mg concentrations in oat were lowest at a soil temperature of 5 °C and highest at 27 °C (Nielson et al., 1960). With 'Sacramento' barley, Power et al. (1970) found that the N concentration was unaffected by soil temperature in the range of 9 to 22 °C at several growth stages. The P concentration was usually highest at 9 °C. The 9 °C soil temperature did, however, slow plant growth compared to two higher soil temperatures.

Under field conditions where early season soil temperatures were lowered by stubble mulch tillage compared to clean seedbed preparation, Smika and Ellis (1971) found that the nutrient content of hard red winter wheat was not affected by soil temperature when plant samples were collected at the same stage of growth (end of tillering, stage 5 and at heading, stage 10.5).

Ambient temperature affects nutrient uptake in rice because of its influence on both plant metabolism and soil processes. Low temperatures decrease the respiratory rate and retard nutrient uptake (Yoshida, 1981). The percentage reduction in nutrient uptake caused by low temperatures is not the same for all nutrients (Takahashi et al., 1955). The inhibitory effects of low temperatures on nutrient uptake by rice suggested by Yoshida (1981) is of the order $\text{PO}_4 > \text{H}_2\text{O} > \text{NH}_4 > \text{SO}_4 > \text{K} > \text{Mg} > \text{Ca}$. High temperatures also retard absorption of NH_4 , PO_4 and K (Baba, 1954).

Studies on plant growth response of rice to Zn at different temperatures have been reported. At a 16 °C temperature, which simulated normal soil temperatures during rice stand establishment in California, greatly reduced dry matter yield and Zn concentration in the shoots were observed (Mikkelsen & Brandon, 1972). Addition of Zn at 16 °C did not appreciably affect Zn concentration or total Zn uptake. However, at 24 °C, Zn concentrations were increased by Zn addition. Cool soil temperatures have frequently been

associated with increased incidence and severity of Zn deficiency on soils low in available Zn (Mikkelsen & Kuo, 1977). Lindsay (1972) suggested two mechanisms for temperature sensitivity for all crops: (i) root elongation and nutrient uptake are diminished in cool soils which reduces the feeding zone of roots and, (ii) the availability of Zn from organic matter is reduced because of reduced mineralization rates in cold soils.

3. Soil Moisture

Soil moisture affects nutrient absorption in several ways. Soil moisture influences the relative concentration of nutrients in the soil solution, plus it affects root growth. Optimum soil moisture environments are dramatically different for rice than for other small grains. Therefore, the effect of soil moisture on nutrient uptake can be markedly different.

Power et al. (1961a) found that dry soil conditions increased N concentration in the aboveground portion of hard red spring wheat at later stages of growth. They (Power et al., 1961b) also observed that the amount of P assimilated by the aboveground portions of spring wheat was not consistently influenced by soil moisture or P fertilization. Boatwright et al. (1964) studied the effect of soil moisture on P uptake by wheat at various growth stages. Plants did not absorb fertilizer P from a dry soil. There was a time lag in P absorption when a dry soil was wetted, especially in older plants. They concluded that little P fertilizer will be used by wheat unless the soil around the fertilizer remains wet for 3 to 4 d.

Karlen et al. (1978) studied the effect of soil moisture on the cation composition of hard red winter wheat emerging from dormancy. Wet soil conditions tended to lower Ca and Mg concentrations in the aboveground tissue at Feekes stage 2, but had no effect on K concentration. In contrast, Letey et al. (1962) showed that Ca and Mg concentrations in barley were not greatly modified by soil O₂ supply.

The influence of soil submergence on the availability of plant nutrients to rice has been summarized by Ponnamperuma (1972). Flooding of the soil and subsequent depletion of O₂ (reduction), results in increased accumulation of NH₃ (Patrick & Mahapatra, 1968; Ponnamperuma, 1972; Shapiro, 1958; Mahapatra & Patrick, 1969; Brandon, 1977; Sah & Mikkelsen, 1986), Fe, and Mn (Sajwan & Lindsay, 1986) in the soil solution and rice plants. In addition, Sajwan and Lindsay (1986) showed that soil submergence reduces Zn availability and uptake because of increased reduction and solubilization of Fe and Mn which have an antagonistic effect on Zn uptake.

The effects of flooding and draining on nutrient availability, particularly P, of rice and crops following rice have been studied by several investigators in recent years. Martin et al. (1971) first suggested that P deficiency in safflower (*Carthamus tinctorius* L.) planted after rice was caused by soil submergence during rice culture. Phosphorus deficiency is common in crops grown in rotation with rice even though the rice crop may show no evidence of P deficiency (Brandon, 1977; Brandon & Mikkelsen, 1979; Sah & Mikkelsen, 1986). These researchers suggested that P deficiency in barley, wheat,

and safflower was caused by increased solubilization of Fe during the flooded cycle (reduced) of rice production, and subsequently, by Fe adsorption of soil-solution P during the early part of the drained cycle (reoxidized). Soil and fertilizer P are rapidly adsorbed by reoxidized amorphous Fe in the drained cycle which renders soil P unavailable to crops following rice (Brandon, 1977). The findings of Willett et al. (1977) in Australia were supported by those of Brandon and Mikkelsen (1979) in California, Singhanian and Goswani (1978) in India, and Griffin and Brandon (1983) in Louisiana. The extensive research on the increase of soil-solution P and P uptake by rice during soil submergence and decrease of soil-solution P and plant uptake by upland crops following rice documents the primary effect of soil moisture on P nutrition in rice-based cropping systems.

4. Other

Soil salinity can also influence plant nutrient concentrations with the effect depending on degree of salinity and the composition of soluble salts. By adding increments of salts to increase soil salinity, Hassan et al. (1970) found the following effects on nutrient concentrations: (i) decreased P, Ca (depending on nature of salinity), Cu, and Fe; (ii) increased Mg, Na, Zn, and Mn; and (iii) increased K at low salinity and reduced K at higher salinity.

The references cited in this section point out the large effects various factors have on the nutrient concentrations in small grains. It is not surprising that much diversity in nutrient levels in small grains has been reported.

B. Plant Factors

Plant species, cultivar, plant maturity, and plant part all have an effect on plant nutrient concentration. Interpretation of plant analysis data must be made taking these factors into consideration.

1. Species Differences

Small-grain species have been shown to differ in nutrient concentration when sampled at similar stages of maturity. Bishop and MacEachern (1971) compared the nutrient concentration of wheat and barley by analyzing the second, third, and fourth leaves from the bottom of the plant when heads were 90 to 100% emerged (stage 10.5). Phosphorus concentrations in wheat leaves were higher than those in barley leaves, while Ca and Mg concentrations in barley were approximately double those in wheat. Nitrogen concentrations in wheat were considerably higher than those found in barley.

Trends of higher Ca concentrations in barley compared to wheat, and higher K levels in oat plants compared to barley or wheat were observed in greenhouse studies (Crooke & Knight, 1971). Concentrations of N, P, Mg, and Mn were similar for the three crops. Five small-grain species were investigated for species effect on Ca, Mg, K, and Na concentrations of seedlings under growth chamber conditions [(S.C. Brubaker, 1979) The effect of soil water and potassium on grass tetany related components of cereal forages.

(M.S. thesis, Kansas State Univ., Manhattan)]. Oat had significantly lower K concentrations than the other four species at most sampling dates while barley and triticale had the highest K concentrations. Oat consistently had the highest Ca and Mg concentrations compared to the other species. Barley was found to have a substantially higher Na concentration.

Baker and Tucker (1971) studied NO_3 accumulation in oat, wheat, barley, and rye forage and concluded that there was little difference in NO_3 accumulation. Nitrate concentration was found to be a function of N and P fertilization and date of sampling.

Brown and Stark (1986) compared the response of three classes of wheat—soft white winter, hard red winter, and hard red spring—for their response to N fertilization. They found that flag leaf N concentration at flowering was a good predictor of N-fertilizer utilization within a location, but found a variety by location interaction that hindered use of flag leaf N as an indicator of wheat N status.

Viets et al. (1954) found little difference in the response of wheat, oat, and barley to Zn fertilization, but did find slightly higher Zn concentrations in the upper leaves of barley at heading. In contrast, Gladstone and Lone-ragan (1967) reported little difference in the concentration of Zn in wheat and barley.

2. Cultivar Differences

Significant wheat and barley cultivar differences in the accumulation of most nutrients, with the exception of Zn, Ca, Mo, and Fe, have been reported by Kleese et al. (1968). The range of nutrient concentrations in the leaves of barley compared to the range in wheat cultivars were similar for the two species. In South Dakota, nutrient concentrations of four barley cultivars sampled at heading (stage 10.2–10.3) contained similar concentrations of N, P, Mg, S, Fe, Zn, and Mn. Potassium concentrations ranged from 15.2 to 20.2 g kg⁻¹ and Ca from 4.4 to 7.9 g kg⁻¹ (Diebert et al., 1968. Unpublished Pamphlet no. 1, Plant Sci. Dep., S. Dakota State Univ., Brookings).

Donohue and Brann (1984) reported only small differences between three soft red winter wheat cultivars for optimum N concentrations for entire above-ground plant samples at Feekes stage 4 and for flag leaf samples (stage 10). They concluded from these locations that a N-sufficiency range of 40 to 50 g kg⁻¹ could be used for samples collected at both growth stages.

Tanaka et al. (1959) and Ward et al. (1973) reported a rather wide range of N content in the leaves of rice cultivars of different maturity. The N concentration in the most recent fully expanded leaves of eight southern USA rice cultivars at the mid-tillering and panicle initiation growth stages ranged from 24 to 50 g kg⁻¹ (Ward et al., 1973). Brandon et al. (1981b) reported the critical N concentrations at panicle initiation in a tall California cultivar, S6, and semidwarf cultivar, M9, were 32.5 and 36.5 g kg⁻¹ of N, respectively. The critical N concentrations in the southern U.S. tall (Lebonnet) and semidwarf (Bellemont) rice cultivars in Louisiana were reported to

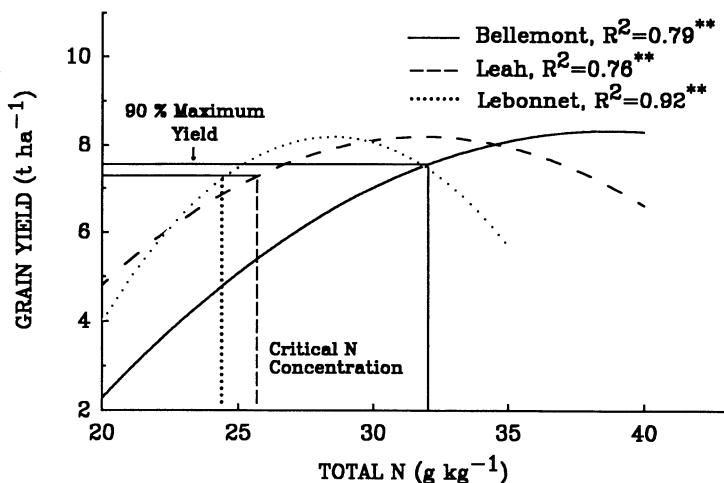


Fig. 19-1. Differences in critical total N levels of tall (Lebonnet) and semidwarf (Bellemont and Leah) rice cultivars at panicle initiation stage of growth.

be 25 and 32 g kg⁻¹ of N (Brandon et al., 1981a), respectively, at the panicle initiation growth stage (Fig. 19-1). Maximum grain yields of the tall and semidwarf cultivars were observed at 28 and 38 g kg⁻¹ of N, respectively, at the panicle initiation growth stage in these studies.

Definite cultivar differences in P absorption, growth, and yield of rice on P-deficient acid soil in Thailand were reported by Koyama et al. (1973). The rice cultivar, Dawk Mali 3, grew better and had greater yields than other cultivars because of higher P absorption. Ponnampuruma (1976) subsequently observed cultivar differences in P absorption and yield of a wide range of cultivars. The effect of Zn deficiency on plant Zn concentrations and yield of different tropical rice cultivars was reported by Yoshida et al. (1973). Their studies showed that cultivars most susceptible to Zn deficiency were less vigorous and had less tillering capacity. Yoshida (1981) reviewed critical, normal, and toxic concentrations of Fe in rice plant tissue. Plant chlorosis induced by Fe deficiency was evident at an Fe concentration of 70 mg kg⁻¹ on a dry matter basis. Plant concentrations > 70 mg kg⁻¹ of Fe were adequate for normal plant growth (Yoshida, 1981). Accumulation of an excessive amount of Fe in rice leaves is characterized by Fe toxicity. Typical symptoms of Fe toxicity may be observed when the Fe content of leaf blades is > 300 mg kg⁻¹ (Tanaka et al., 1966). Yoshida (1981) reported differences among 12 rice cultivars in their ability to absorb Fe. Ponnampuruma (1976) showed that tropical rice cultivars also differ in their tolerance of Fe toxicity.

Cultivar and species effects on nutrient concentration in small grains exist. There are, however, several studies showing that the differences between cultivars are relatively small. For example, Ylaranta et al. (1979) found no clear differences in the micronutrient contents between spring and winter wheats over the entire growing season, while Engel and Zubriski (1982) reported significant differences in N contents of different cultivars for some

years but not others. The data indicates that species and cultivar effects cannot be taken for granted and must be investigated before recommendations are made and critical values established. This seems especially true as high-yielding cultivars are developed through introduction of germplasm from sources outside the traditional genetic pool.

3. Growth Stage and Seasonal Variation

The use of plant analysis to diagnose nutrient deficiencies can be grossly misinterpreted if the user does not understand the variation in nutrient concentrations that can occur as a function of growth stage and between growing seasons. Researchers in Europe, using plant analysis for determining the second N dressing for 723 000 ha of winter cereals (Neubert et al., 1977), revealed that site and variety have a small influence on the relationship between plant N and yield of wheat, barley, and rye, as compared to seasonal weather conditions. Beringer and Hess (1979) found that the total N content could vary by 40% within a week's time in the early stages of growth, indicating the sensitivity of N concentration to environmental conditions. Ylaranta et al. (1979) sampled spring and winter wheat twice a week during the growing season to obtain information on seasonal micronutrient variations. The highest content of B, Cu, and Fe were recorded early in the stage of growth, followed by a rapid decrease towards the end of the growing season. Boron decreased from 4 to 12 mg kg⁻¹ to <2, Cu from 6 to 10 mg kg⁻¹ to 3 to 4, and Fe from 80 to 210 to 30 to 75 mg kg⁻¹. Manganese tended to increase in concentration towards harvest. The behavior of Zn content was different from other micronutrients, exhibiting a slight tendency to increase in the latter growth stages. A rapid drop in N content of spring wheat was reported between Feekes growth stage 3 to 10.5, with a curvilinear decrease between stages 5 to 10.5 and a linear relationship at stage 3.

The references point out the importance of evaluating variations within a season as well as between seasons in interpreting plant analysis data of small grains. Failure to consider these factors will lead to misinterpretations.

III. SAMPLING FOR PLANT ANALYSIS

The usefulness of plant analysis to assess the nutritional status of small grains largely depends on sampling procedures. Information provided by plant analysis is only as representative as the samples collected. Plant growth stage and part of the plant sampled have a tremendous influence on nutrient concentration. Several stages of growth and plant parts have been used by various researchers, but no stage of growth and plant part has been found superior for all nutrients with all small grains.

A. Stage of Growth

Small grains have been sampled from tillering (stage 3) to boot (stage 10) or early head emergence (stage 10.3). With wheat, oat, and barley,

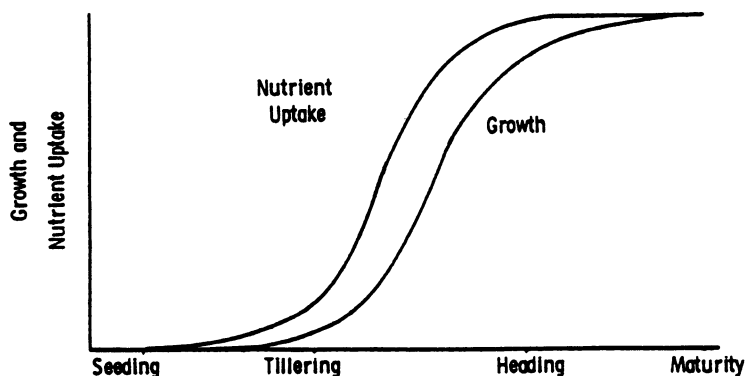


Fig. 19-2. Typical relative growth and nutrient uptake curves for small grain crops.

sampling at tillering may allow time for correction of nutrient deficiencies on the current crop. Boot and early head emergence sampling is normally too late in the season for correction of nutrient deficiencies on the existing crop.

A typical growth and development curve for small grains is shown in Fig. 19-2. Nutrient uptake precedes dry matter accumulation with a rapid increase in nutrient and dry matter accumulation occurring between tillering and head emergence. Plants sampled at heading (stage 10.3-10.4) should reflect the nutrient sufficiency at the time flowering is completed. The nutrient concentrations in plants generally decline between tillering and heading.

Critical nutrient concentrations change with stage of plant development. Therefore, it is advantageous to collect multiple samples for monitoring N-fertilizer requirements. Sampling rice between tillering and panicle differentiation provides tissue analysis results early enough for corrective N fertilization (Mikkelsen, 1983). To obtain maximum precision, it is desirable to collect a series of rice leaf samples, preferably at: (i) mid-tillering stage (40-50 d after planting for 140- and 150-d cultivars, respectively); (ii) maximum tillering stage (50-60 d after planting); (iii) panicle initiation stage (60-80 d after planting); and (iv) panicle differentiation stage (70-90 d after planting) (Brandon et al., 1981a; Mikkelsen, 1983).

Growth stage is an important factor in interpreting plant analysis data. Care should be taken to ensure that nutrient concentrations from plants are interpreted accurately with critical levels at the proper growth stage. Improper growth stage identification can result in errors in interpretation.

B. Plant Part

When sampling wheat, barley, and oat plants at tillering (stage 3), the entire aboveground portion of the plant should be sampled. At heading (stage 10.3), either whole plants, upper leaves, or flag leaves are commonly sampled.

Nutrient concentration differences have been shown between plant parts sampled at the same growth stage. Flag leaves of hard red winter wheat sampled at heading (stage 10.3) had nearly twice the N concentration as whole aboveground plant samples at the same stage (D.A. Whitney and G.A. Peterson, 1971, unpublished data), while P and K concentrations were essentially the same. Similar results were observed for oat in South Dakota (J.H. Pfeifer, 1971, unpublished data).

The influence of plant part on nutrient concentrations in rice has been reported. Large differences in nutrient concentrations occur between the most recently matured leaf and the whole plant (Westfall et al., 1973; Ward et al., 1973). Thenabadu (1966) established that the first and second most fully expanded leaves were the most sensitive indicators of the N status of rice. However, the most recently matured leaf, commonly referred to as the Y leaf, has been shown to be the best indicator of N status (Brandon et al., 1980; Hafez & Mikkelsen, 1981; Mikkelsen, 1983; Ward et al., 1973; Wallihan & Moomaw, 1967). This leaf tends to be erect, which makes sampling easier and more accurate. The Y leaf is widely used for determining the nutrient status of commercial rice crops.

C. Sample Size

Sample size for plant analyses must be large enough to provide a representative sample of the crop and sufficient dry matter for chemical analysis. Sampling procedure to minimize sample variability has been delineated, but limited research information is available on optimum sample size for wheat, barley, and oat. Chapman (1964) suggests 200 or more leaves are required for a good sample. For whole-plant samples at heading, most guidelines are for 20 to 30 plants taken randomly across the field (Jones et al., 1971; Whitney et al., 1985). Collection of 50 to 100 Y leaves from rice plants in early stages of plant development, from 30 to 60 locations within a field, provides sufficient dry matter and minimizes variability if crop growth is uniform. A sample of 30 to 60 individual Y leaves is sufficient in later stages of plant development.

Weisset et al. (1982) studied the variation in plant results as influenced by sampling pattern and sample size in 20 winter grain fields ranging in size from 34 to 109 ha. When a sample was evenly taken (one sample ha^{-1}), the coefficient of variation in total N content was 10 to 12%. They concluded that the traditional zig-zag route is not necessary. The sampling area should be no larger than 50 ha. Regardless of the sampling route used, it should be marked when multiple sampling procedures are to be collected. Separate samples should be taken from atypical areas characterized by abnormal plant growth, plant symptoms, plant nutrient status, or other specific problems. Close observation of the crop and judgment based on experience should be used in determining the size of the sampling area represented by a sample and the number of samples required in a field. The more subsamples collected, the more likely the sample will represent the field.

IV. DIAGNOSING NUTRIENT DEFICIENCIES

A. Diagnostic Approach

Information cited above indicates that large variations can exist in nutrient concentrations in plants due to soil-plant-environment relationships. Use of plant analysis to help diagnose problems that exist in a certain area of a field can be a valuable tool. This technique is termed the *diagnostic approach* of plant analysis. Samples should be collected as soon as poor growth or nutrient-deficiency symptoms become evident. Deficiency symptoms of N, P, and Zn usually become visible in small grains at early stages of growth. Plant samples should be collected from both the field area where plant symptoms are apparent and areas where plants appear normal. A sample from transitional areas between the two extremes may be useful in diagnosing the problem. Soil samples from the same area should be analyzed to increase the accuracy of plant analysis interpretation. Simple and rapid soil analysis parameters, such as pH and salinity, often reveal the soil factors that can be identified with plant growth problems. Information about fertilization, weed and insect control, tillage, and climatic conditions should be recorded. These factors often have a major influence on plant growth problems. Comparison of the nutrient concentration in plant and soil samples from the two contrasting areas in the field can be extremely helpful in pinpointing the nutrient disorder that has resulted in poor growth. However, caution should be exerted because plant symptoms that are similar to nutrient-deficiency symptoms can be caused by insects and diseases. Plant roots should always be examined to ensure that they are developing normally and insects or diseases have not adversely affected root development, thereby limiting nutrient uptake.

The diagnostic approach will often provide answers to plant nutritional problems that are difficult to analyze by other means. For example, in California, rice researchers (Mikkelsen & Brandon, 1975; Mikkelsen & Kuo, 1977) used the diagnostic approach to identify Zn deficiencies that usually occurred in only parts of the field. However, Westfall et al. (1971) reported that Zn and Fe chlorosis were corrected by Zn and Fe application to rice, but the concentration of Zn and Fe in the plant was not increased.

B. Monitoring Approach

Collecting plant samples at a given stage of development and comparing the plant analyses with established deficiency levels is called the *monitoring approach* to plant analysis. This approach requires that specific guidelines be followed in respect to species and cultivar, growth stage, plant part sampled, and environmental conditions. Over the past years, progress has been made in establishing critical levels, but it is difficult to give generalized critical levels that are applicable to broad geographic regions. The importance of cultivar variation is not well understood and has not been well documented for the small grains. Chapman (1966) demonstrated the variation in re-

ported critical nutrient levels. More recently, Reuter and Robinson (1986) conducted an extensive literature review and summarized the various concentration ranges reported in the literature, from critical to toxic, of various nutrients for a wide range of crops. Again, their data point out the large variations in critical nutrient concentrations that had been reported by researchers throughout the world. For this reason, it is impossible to report one critical concentration level for a specific plant nutrient that is applicable to a wide geographic region of diverse environments. The authors of this chapter, therefore, are reporting critical nutrient levels that have been found to be generally acceptable for specific regions. The transfer of critical levels from one region to another should be done with caution, and preferably only after field verification has been conducted.

Traditionally, total N concentrations have been used in the monitoring approach. However, recently there has been an interest in the use of stem NO_3 in monitoring the N status of small grains. Gardner and Jackson (1976) in Arizona found that the $\text{NO}_3\text{-N}$ concentration of the lower 5 to 8 cm of the stem was a good indicator of N status of the wheat plant. The sufficiency ranges proposed were 7000 to 12 000 mg kg^{-1} of $\text{NO}_3\text{-N}$ at the 3 to 4 leaf stage, 5000 to 10 000 mg kg^{-1} at the jointing stage, and 3000 to 9000 mg kg^{-1} at the boot stage of growth. Nitrogen concentrations lower than these would indicate a need for N-fertilizer applications. Levels greater than those may result in reduced yields due to excessive N availability. Visual N deficiency symptoms appeared as stem $\text{NO}_3\text{-N}$ levels dropped to 2000 mg kg^{-1} . The determination of P in the lower portion of the wheat stem was not found to be suitable for indicating the P status of the crop. Brown and Jones (1979) reported that the $\text{NO}_3\text{-N}$ concentrations necessary for maximum production should be at least 3500 mg kg^{-1} at the 3 to 4 leaf stage and 1000 mg kg^{-1} at jointing. Beringer and Hess (1979) found that the correlation between grain yield and NO_3 content of the stem became low after the tillering stage. However, Papastylianou (1986) found a high correlation between dry matter production and stem NO_3 . Stem NO_3 was more sensitive than total leaf N as an indicator of N nutrition status of barley when samples were collected at the tillering stage of growth. Based primarily upon results of Brown and Jones (1979), Dow (1980) published critical nutrient ranges for stem NO_3 of small grains in the Pacific Northwest (Table 19-1). These levels correspond well with those reported by Gardner and Jackson (1976) in Arizona. The critical nutrient ranges of other nutrients for small grains in the Pacific Northwest are also reported in Table 19-1. Dow defined the critical nutrient range (CNR) to be "that range of concentrations above which we are reasonably sure the crop is amply supplied and below which we are reasonably sure the crop is deficient." Thus, within the CNR is a range of uncertainty. Dow points out that the accuracy of prediction is enhanced by monitoring, i.e., by taking samples periodically during a growing season. Seasonal monitoring then considers the changes in nutrient levels during the growing season. The approach of comparing across years in a particular environment can be useful in establishing critical nutrient levels for various crops that are regionally and environmentally specific.

Table 19-1. The critical nutrient range (CNR) for small grains in the Pacific Northwest (Dow, 1980).†

Nutrient	Growth stage‡	Plant part	CNR
<u>Wheat</u>			
N	Joint (GS 6)	Total tops	25-30 g kg ⁻¹
	Boot (GS 10)	Top two leaves	23-27 g kg ⁻¹
NO ₃ -N	3-4 leaf (GS 2)	Underground stem	2.5-3.5 g kg ⁻¹
	Jointing (GS 6)	First 2 in. aboveground	0.8-1.5 g kg ⁻¹
P	12 wk (GS 4)	Total tops	3.0 g kg ⁻¹
	Jointing (GS 6)	Total tops	3.2-4.0 g kg ⁻¹
	Early boot (GS 9)	Total tops	1.5-2.0 g kg ⁻¹
K	Jointing (GS 6)	Total tops	20-25 g kg ⁻¹
	Early boot (GS 9)	Total tops	15-20 g kg ⁻¹
<u>Barley</u>			
NO ₃ -N	3-4 leaf (GS 2)	Below-ground stem	0.6-0.7 g kg ⁻¹
Mn	Early tillering (GS 2.5)	Flag leaf	18-20 mg kg ⁻¹
Cu	Tillering (GS 3)	Leaves	4.0 mg kg ⁻¹
<u>Oat</u>			
NO ₃ -N	3-4 leaf (GS 2)	Below-ground stem	0.6-0.7 g kg ⁻¹
Mn	Early tillering (GS 2.5)	Flag leaf	22-25 mg kg ⁻¹

† Prepared by the Northwest Soil and Plant Testing Work Group.

‡ Approximate Feekes scale growth stage.

The sufficiency range for wheat in the southern USA, specifically taken from data of Plant (1988) in Georgia, are presented in Table 19-2. These researchers have been able to establish sufficiency ranges for several nutrients over a wide range of growth stages for wheat.

Nutrient levels for wheat, oat, and barley for the Great Plains of the USA are shown in Table 19-3. These levels have been previously reported by Ward et al. (1973). Those values in Table 19-3 are for a late growth stage, and little yield response would be expected from nutrient application at this time. More recently, Vaughan et al. (1989) reported critical N levels for hard red winter wheat in the western Great Plains region (Table 19-4). Suggested critical N levels are given for total N and stem NO₃-N. However, the "best" N recommendation model was found to be the spring-available soil NH₄-N plus NO₃-N to 60-cm soil depth and Feekes 5 leaf N concentration. This model was accurate at low required N rates, but more conservative at higher N rates. Vaughan et al. (1989) found it difficult to use tissue analysis alone as a predictive tool because of geographic and environmental variability, thus, the reason for the necessity to include spring soil N data. The variability in stem NO₃-N values were large and the use of this plant parameter was not as accurate as total N tissue values. This resulted in large "transitional concentrations" in stem NO₃-N in Table 19-4.

A considerable amount of work has been conducted on S deficiencies of small grains in Australia. The critical S levels proposed by Spencer and Freney (1980) are presented in Table 19-5. The use of SO₄-S and total S as an indicator of nutrient sufficiency has met with varied success. However,

Table 19-2. The sufficiency range for wheat in Georgia (Plank et al., 1988).

Nutrient	Growth stage†	Plant part	Sufficiency range, g kg ⁻¹
N	GS 3	Whole plant	40-50
	GS 4-6	Whole plant	35-45
	GS 7-8	Whole plant	30-40
	GS 9-10	Whole plant	25-35
	GS 10	Flag leaf	35-45
P	GS 3-5	Whole plant	4-7
	GS 6-10	Whole plant	2-4
	GS 10	Flag leaf	3-5
K	GS 3-4	Whole plant	32-40
	GS 5-8	Whole plant	20-35
	GS 9-10	Whole plant	18-30
	GS 10	Flag leaf	20-30
Ca	GS 3-10	Whole plant	2-5
	GS 10	Flag leaf	3-5
Mg	GS 3-10	Whole plant	1.5-5.0
	GS 10	Flag leaf	2-6
S	GS 3	Whole plant	2.2-5.5
	GS 4-6	Whole plant	1.9-5.5
	GS 7-8	Whole plant	1.7-5.5
	GS 9-10	Whole plant	1.5-4.0
	GS 10	Flag leaf	1.9-5.5
— mg kg ⁻¹ —			
Mn	Unspecified	Whole plant	35-475
Fe	Unspecified	Whole plant	25-100
B	Unspecified	Whole plant	3-20
Cu	Unspecified	Whole plant	5-25
Zn	Unspecified	Whole plant	15-70
Al	Unspecified	Whole plant	<200

† Feekes scale growth stage.

Table 19-3. Interpretation of plant analysis for oat, wheat, and barley based on aboveground samples collected as the head emerges from the boot (GS 10.1) in the Great Plains of the USA (Ward et al., 1973).

Nutrient	Deficient	Low	Sufficient	High
g kg ⁻¹				
N (Winter grain)	<12.5	12.5-17.5	17.5-30	>30
(Spring grain)	<15.0	15-20	20-30	>30
P	<1.5	1.5-2	2.0-5.0	>5
K	<12.5	12.5-15	15-30	>30
Ca (Except barley)		<2	2-5	>5
(Barley)		<3	3-12	>12
Mg		<1.5	1.5-5	>5
S		<1.5	1.5-4	>4
mg kg ⁻¹				
Mn	<5	5-24	25-100	>100
Zn		<15	15-70	>70
Cu		<5	5-25	>25

Table 19-4. Suggested critical N concentration for hard red winter wheat in the Western Great Plains (Vaughan et al., 1990).

Feekes growth stage	N form	Plant part	Units	Critical level	Transition concentration†
3	Total N	Aboveground‡	g kg ⁻¹	40	
5	Total N	Aboveground	g kg ⁻¹	32	25-33
5	Total N	Leaf§	g kg ⁻¹	38	34-38
5	NO ₃ -N	Stem	mg kg ⁻¹	866	639-2750
7	Total N	Aboveground	g kg ⁻¹	27	19-27
7	Total N	Leaf	g kg ⁻¹	35	34-41
7	NO ₃ -N	Stem	mg kg ⁻¹	619	

† The "medium" range where sufficiency and deficiency could coexist.

‡ Aboveground plant material.

§ Two most fully developed leaves.

Table 19-5. The critical S level in wheat in Australia (Spencer & Freney, 1980).

	Growth stage		
	GS 2	GS 5	GS 7
Sulfate S (g kg ⁻¹)	140	120	110
Sulfate S conc. (mg kg ⁻¹)	400	360	190
Total S conc. (g kg ⁻¹)	3	2.8	1.5
N/S ratio	15	16	19

Table 19-6. Critical and adequate concentrations of N in "Y leaves† of southern U.S. grown rice cultivars at different plant growth stages, Crowley, LA.

		Total N, g kg ⁻¹			
Rice cultivar by maturity	Grain type	Panicle initiation		Panicle differentiation	
		Critical‡	Adequate	Critical‡	Adequate
Very early group					
Labelle	Long	28-30	30-35	23-25	25-30
L-201	Long	25-27	26-30	20-22	22-27
M9	Medium	25-27	26-30	20-24	24-28
M-201	Medium	30-32	32-35	25-27	27-31
Early group					
Lebonnet	Long	26-28	28-31	22-24	24-28
Lemont	Long	30-32	32-35	26-28	28-32
Belmont	Long	32-34	34-38	28-30	30-34
Saturn	Medium	24-26	26-28	20-22	22-24
Mars	Medium	26-28	28-32	22-24	24-28
Brazos	Medium	26-28	28-32	22-24	24-28
Mid-season group					
Starbonnet	Long	25-27	27-32	22-24	24-28
Newbonnet	Long	26-28	28-30	24-26	26-28

† Kjeldahl N on dry wt. basis of most recently matured leaves.

‡ Plants with critical concentration of N produced 90% of maximum yield.

Table 19-7. Critical and adequate concentrations of N, P, and K in medium- and short-grain rice cultivars at different plant growth stages in California.

Plant growth stage	Total N, g kg ⁻¹		Extractable PO ₄ -P, mg kg ⁻¹		Extractable K, g kg ⁻¹	
	Critical	Adequate	Critical	Adequate	Critical	Adequate
Mid-tillering	38-40	40-48	1000	1000-1800	14	14-28
Maximum tillering	34-36	36-42	1000	1000-1800	12	12-24
Panicle initiation	30-32	32-36	800	800-1800	10	12-24
Flag leaf	26-28	28-32	800	800-1800	10	12-22

† Analysis on dry wt. basis of most recently matured leaves for Kjeldahl N, 20 g kg⁻¹ of HAc-extractable PO₄-P and K.

the N/S ratios have been found to be less affected by environmental factors. Rassmussen et al. (1977) and Wells et al. (1986) have revealed the N/S ratio proposed by Spencer and Freney (1980) are applicable to many environments under which wheat is grown in the USA.

The critical and adequate concentrations of N in the Y leaf of rice cultivars grown in the southern USA are shown in Table 19-6 for the panicle initiation and differentiation stages of growth. Critical and adequate concentrations of N, P, and K in rice cultivars grown in California are shown in Table 19-7. A more rapid decline in nutrient concentrations over time can be expected if the soil has low levels of residual fertilizer nutrients while a gradual decrease of plant nutrient concentration, as a function of plant development, is typical in soils with high levels of residual N, P, and K.

Monitoring the nutritional status of small grains is a valuable tool in establishing the optimum amount of fertilizer required for optimum yield. A well-planned program of plant analysis permits identification of adequate levels of fertilizer required for optimum yields when used with fertilization and cropping history. Plant analysis may also prevent costly application of excessive amounts of nutrients or applications of nutrients not needed. It should be remembered that identification of nutrient deficiencies late in the growing season may be so late in the plant's stage of development that application of the deficient nutrient may not result in maximum return to the fertilizer investment. Therefore, the monitoring approach must encompass both preplant or in-season soil testing, as well as plant nutrient monitoring during the early stages of growth.

C. New Techniques

Some new techniques to aid in the interpretation of plant analysis have been suggested recently. Brooks and Reisenauer (1985) found that soluble reduced N, expressed as a fraction of the protein N, was a useful predictor of relative growth rate. Leigh and Johnston (1983a, b, 1985, 1986) have reported the usefulness of expressing concentrations of P and K on the basis of tissue water. Less variation during the growing season occurs in the concentration of these two elements if they are expressed on the basis of con-

centration in the tissue water. However, they concluded that N concentrations based on this method are unlikely to be useful in determining the N requirements of barley and that N% in the dry matter was more useful. When K concentrations were calculated on the basis of tissue water, they remained relatively constant during vegetative growth and then increased when water loss was rapid during senescence. Also, whereas K concentrations in the dry matter were affected by the supply of N, P, K, and water, those concentrations based upon tissue water content were influenced only by K supply. Similar relationships were reported for P.

D. Quick Test

The use of a "quick test" for assessing plant nutrient status can be a useful tool for spot-checking fields when laboratory facilities required for more accurate analysis are not readily available. Different degrees of success have been reported by various investigators using quick tests. Guettinger and Koehler (1963) reported that a quick $\text{NO}_3\text{-N}$ test on winter wheat was related to the available soil N and could be used to determine top-dress needs of the crop. The quick test results were closely related to total N in the plant material. Hart and Pettygrove (1985) used commercially marketed "EM Quant Test Strips" as a method of field assessment of the N status of wheat. The test strips were able to separate high from low levels. They concluded the strips were useful in evaluating the amount of NO_3 in wheat plants, and that this method could be used in other situations where critical levels have been previously established for a cultivar at a particular stage of growth. However, the test strips were not effective in determining the NO_3 concentration when the wheat plant was under moisture stress or if the samples were allowed to dry slightly before testing.

A quick test for N in rice tissue is currently used in California to determine N status. Hafez and Mikkelsen (1981) and Mikkelsen (1983) evaluated an Orange-G colormetric method for protein determination in rice leaves. The amount of dye absorbed by dry, ground Y leaves at three stages of rice development was highly correlated ($r^2 = 0.81\text{--}0.98$) with percent N as determined by the Kjeldahl method. They found that 0.2 g of plant material and a 20-mL dye ratio was best correlated with Kjeldahl N if one regression equation was used for all stages of rice plant growth. The Orange-G dye method is a rapid, simple, inexpensive, and acceptable method for determining the N status of rice. This test may be substituted for the Kjeldahl method in monitoring N concentration changes in rice and in determining N fertilizer requirements in mid-season.

V. PRACTICAL APPLICATIONS OF PLANT ANALYSIS

Plant analysis can be useful in diagnosing plant nutrient deficiencies and toxicity problems of small grains when used in combination with soil analysis, plant symptomology, and experience. An effective plant nutrient monitor-

ing program will identify specific plant nutrients required and their optimum rates over time for maximum economic yield. However, under most situations, plant analysis is not as effective in guiding fertilizer usage on annual crops as is soil testing. Soil testing provides an opportunity for the producer to identify potential nutrient deficiencies before planting, thereby ensuring that plants do not become deficient early in the growing season. Plant analysis allows in-season monitoring and adjustment, and thus ensures optimum nutrient relationships during the entire growing season. Wide use of both soil testing and plant analysis will be beneficial to most producers. However, care should be taken to ensure that plant analysis results are interpreted from appropriate data that are applicable to the crop and growing environment.

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Chapter 20

Plant Analysis as an Aid in Fertilizing Corn and Grain Sorghum¹

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The literature probably contains more plant analysis data for corn (*Zea mays* L.) than for any other field crop, a marked contrast to that available for grain sorghum [*Sorghum bicolor* (L.) Moench] which is quite limited. Although many researchers have used data for corn to evaluate plant analyses for grain sorghum, such evaluations have been questioned. Lockman (1972a, b) found minimal differences between the analyses of the whole tops of corn and sorghum seedlings. Differences, however, increased as growth progressed. Bennett (1971) also indicated that corn plant analysis data should not be used to evaluate grain sorghum plant analyses. As more data become available, such as that compiled by Reuter and Robinson (1986), grain sorghum should be treated separately from corn. However, because the two crops contain similar amounts of most elements and because the literature related to grain sorghum is scant, this chapter treats the two crops similarly unless specific data are available that distinguish between the two.

Plant analysis has only recently come into its own as a technique for evaluating field nutrient problems. Tyner (1946) proposed critical N, P, and K values for corn leaf analyses some years ago. Several books, bulletins, and review articles have been written on plant analysis (Goodall & Gregory, 1947; Lundegardh, 1951; Ulrich, 1952; Wallace, 1956; Reuther, 1960; Smith, 1962; Chapman, 1966; Wallace, 1961; Hardy, 1967; Greer, 1970; Bates, 1971; Davidescu & Davidescu, 1972; Jones, 1974; Reisenauer, 1978; Jones, 1984a, Reuter & Robinson, 1986; Martin-Prevel et al., 1987). Much of the current surge in interest in the plant analysis technique stems from the rather significant developments in methods for conducting the laboratory assay of plant

¹Contribution from the Univ. of Georgia, Athens, GA, the USDA Conserv. and Production Res. Lab., Agric. Res. Serv., Bushland, TX, and Iowa State Univ., Ames, IA.

tissue. Atomic absorption, flame emission, and direct reading spark and plasma emission spectroscopy have greatly simplified analytical procedures. Analyses for most of the essential elements can be made quickly and at relatively low cost. Plant analysis services to farmers in the USA are being provided by an ever-increasing number of state-supported and commercial laboratories. Surveys conducted by the USDA-Extension Service (Jones, 1985) since 1980 have found that approximately 500 000 plant tissue samples are being assayed annually for farmers.

Goodall and Gregory (1947) found that research related to plant analysis could be classed into four categories: (i) investigation of nutritional disorders manifested by definite symptoms, (ii) interpretation of the results of field trials, (iii) development of rapid testing methods for use in advisory work, and (iv) use of plant analysis as a method of nutritional survey. These categories are still applicable today. Practical application of the plant analysis technique in the field primarily relates to confirming suspected elemental deficiencies or toxicities, monitoring the crop to uncover significant changes in elemental composition which could lead to deficiencies or excesses (Jones, 1983), and predicting fertilizer needs (Baker et al., 1966). An interesting application of the plant analysis technique yet to be fully exploited is the evaluation of genetically controlled element uptake and utilization (Munson, 1969).

Although their utilization is quite different, plant analysis has frequently been compared to soil testing in field application. The plant's ability to absorb an element from the soil solution is reflected in the concentration of the element in the plant or in one of its specific parts. Therefore, a plant analysis can be a means of measuring the soil-plant nutrient element environment. Along these lines, Krantz et al. (1948) gave four principal objectives for a plant analysis: (i) to aid in determining the nutrient-supplying power of the soil, (ii) to aid in determining the effect of treatment on the nutrient supply in the plant, (iii) to study the relationship between the nutrient status of the plant and crop performance as an aid in predicting fertilizer requirements, and (iv) to help lay the foundation for approaching new problems or surveying unknown regions to determine where critical plant nutritional experimentation should be conducted.

None of these objectives fits the current use of plant analysis. Today, most farmers use it primarily to diagnose suspected essential element insufficiencies. The second most common use for the plant analysis is probably best described by Objective iii, although it is usually limited to use with fruit and nut trees. Munson and Nelson (1973) describe three uses for a plant analysis, verification of deficiency symptoms, for comparing assays of normal vs. abnormal plants, and for crop logging. Each one is an important application for a plant analysis result.

Although most soil tests give reliable information regarding the supply of plant-available nutrients in the soil, they are indirect measures of the sufficiency of nutrients in plants and, thus, have limited usefulness in diagnostic situations. Plant analysis gives direct information and, when properly interpreted, is the most reliable diagnostic test. However, when used together, the combined results can effectively evaluate the sufficiency of the soil-plant

nutrient status to satisfy the crop requirement, and can form the basis for specifying needed corrective treatments (Jones, 1986).

The plant analysis technique involves a sequence of steps from sampling to sample preparation and laboratory analysis, and then to an interpretation of the laboratory result. Each step requires particular skill by the user. The desired plant part must be properly identified and collected; decontaminated, if necessary; and prepared for analysis without contaminating or altering its chemical content. Interpretation of an analysis is to some degree an acquired art, gained from experience on how best to apply known interpretative values to evaluate a particular analysis result. This chapter is a review of the current state of the art for the plant analysis technique when specifically applied to corn and grain sorghum.

I. SAMPLING

The validity and usefulness of a plant analysis hinges on the care and method used to obtain the required plant tissue sample. Unfortunately, less research has been devoted to sampling than to other aspects of the plant analysis technique; yet sampling, if not properly done, can invalidate the analysis result.

Plant part selected and time of sampling must correspond to the best relationship that exists between element concentration and physical appearance of the plant or yield (Bates, 1971). It means selecting a specific part at a specific location on the plant and at a definite growth stage. The number of parts, such as leaves, to collect per plant and the number of plants chosen for sampling deserve careful consideration. For both corn and grain sorghum, only one leaf per plant is normally collected. However, the number of plants from which a tissue sample is to be taken is dictated by the condition of the plants. Steyn (1961) observed that to obtain representative samples, plants in poor condition required more intensive sampling than those free from nutritional stress. Consequently, he recommended taking samples from as many plants as practical.

Most elements are not evenly distributed in the corn leaf blade (Sayre, 1952). Jones (1970) found that certain elements tend to accumulate in the leaf margins while some element concentrations are lower in the midrib than those found in the leaf blade. Therefore, an elemental content assay of the entire leaf could be affected by the shape of the leaf blade. An analysis of a typical corn leaf and its components are given in Table 20-1. Chapman (1964) must have recognized this problem of uneven elemental distribution in the corn leaf because he suggested that only the mid-third section of the leaf be analyzed to minimize the influence of margin and midrib contents on a whole-leaf analysis. Although Chapman's sampling procedure is worthy of adoption, all of the significant interpretative data for corn are given based on a whole-leaf analysis. In light of this heterogeneous distribution of elements in the corn leaf, it is important that a leaf sample consists of the entire leaf or a major portion of it. Sumner (1977b) found that the entire, or

Table 20-1. Distribution of 14 elements in the various parts of a corn ear leaf at the time of stilk (Jones, 1970).

Element	Whole ear leaf	Leaf part		
		Margin†	Blade	Midrib
		g kg^{-1}		
N	25.4	25.8	25.0	7.4
P	2.7	2.9	3.2	1.4
K	16.8	12.1	17.3	18.2
Ca	8.0	9.0	8.8	4.2
Mg	5.6	3.9	6.2	5.5
		mg kg^{-1}		
Al	95	88	99	52
B	14	51	8	6
Ba	8	6	8	11
Cu	11	12	12	8
Fe	148	181	171	79
Mn	146	272	124	70
Mo	2.6	2.0	3.0	2.5
Sr	30	22	28	27

† Consists of the 4-mm part along the edge of the leaf.

at least three-quarters, leaf must be taken from the middle of the corn plant if a valid interpretation is to be made using the Diagnosis and Recommendation Integrated System (DRIS) interpretative method.

The specific sampling procedures for corn and grain sorghum are quite different because of the nature of the two species. Historically, the plant part designated for sampling was probably selected more on the basis of its ease of identification than on the significance of its composition as related to either the plant's appearance or yield. Sampling procedures for many crops, including corn and grain sorghum have been described by Jones et al. (1971). Specific sampling procedures for both crops are given in Table 20-2.

In a diagnostic situation when a nutrient element insufficiency is suspected, it is advisable to collect, and keep separate, identical tissues from

Table 20-2. Sampling procedures for corn and grain sorghum.

Crop	Plant part	Time of sampling	No. of plants to sample
Corn or grain sorghum	Whole aboveground portion of plant	Seedling stage, < 30 cm (12 in.) tall	20-30
Corn or grain sorghum	The entire, fully developed leaf below the whorl	Prior to tasseling or heading stage	12-25
Corn†	The entire leaf at the ear node (or immediately above or below it)	From tasseling to the silk initiation	12-25
Grain sorghum†	Second leaf from the top of the plant	At heading	15-25

† Recommended sampling procedure when determining nutrient status of plant as it relates to fertility status of the soil, fertilizer treatments, and yields.

both affected as well as nearby normal-appearing plants so that a comparison of analysis results can be made as suggested by Munson and Nelson (1973). However, there is some danger in this approach if the affected plants have been in that condition for an extended period (Jarrell & Beverly, 1981). Therefore, considerable care is required when selecting plants for sampling to ensure that both stage of growth as well as degree of development are reasonably similar, and that similarly mature leaf tissue exists for sampling.

There are as many instructions on what not to sample as on what to sample. Sampling is not recommended when the plant part is soil or dust covered, damaged by insects, mechanically injured, or diseased. Dead plant tissue should not be included in collected samples. In addition, sampling is not recommended when plants have been under prolonged moisture or temperature stress.

Seed is not normally a useful plant part to assay for determining the nutritional status of the sampled plant. Although the element concentration in the grain can be affected by fertilizer treatment and the nutrient status of the plant, grain yield is usually affected more than grain composition. Also, little interpretative data is available based on the elemental content of grain, with the exception of the work by Pierre et al. (1977a, b) and Russell and Pierre (1980) who studied the relationship between corn grain yield and the N content of the grain.

II. SAMPLE PREPARATION AND ANALYSIS

This topic is covered in more detail in chapter 15 of this book (Jones and Case). However, it may be well to discuss some of the procedures that apply specifically to the analysis of corn and grain sorghum plants and their leaf tissues.

A. Decontamination

Decontamination by washing plant and leaf tissue is not necessary unless the plants are unusually dusty or coated with spray residues. If Fe is an element of interest for determination, the tissue *must be* washed (Jones, 1963; Baker et al., 1964; Wallace et al., 1980). Surface-irrigated plants, or those growing under negligible rainfall conditions, require washing. Plants growing under normal rainfall conditions probably would not require washing. Steyn (1959) recommended washing fresh leaf material with a mild 0.1 to 0.3% detergent solution and then rinsing in pure water. Similar decontamination procedures have been described by Wallace et al. (1980), and Sonneveld and van Dijk (1982). Jacques et al. (1974) reported that washing grain sorghum plant tissue parts with deionized distilled water reduced Fe concentrations of blade, sheath, and head tissue but did not affect Ca, Cu, Mg, Mn, and Zn concentrations in the tissue.

Washing should be done quickly to avoid long periods of contact between the washing solution and plant material that can lead to leaching of

Table 20-3. Element concentration found between washed and unwashed corn leaves.

Element	Baker et al. (1964)		Jones (1963)	
	Unwashed	Wiped with detergent solution	Unwashed	Washed in distilled water
	g kg^{-1}			
Ca	8.7	8.5	4.8	4.5
K	20.4	21.7	12.2	12.6
Mg	1.6	1.6	3.9	4.1
N	--	--	29.8	31.1
P	2.7	2.9	2.2	2.2
	mg kg^{-1}			
B	17.2	17.0	11	10
Cu	29.5	28.8	9	10
Fe	136	134	96	85
Mn	--	--	73	64
Mo	--	--	1.1	1.2
Zn	23.1	30.5	22	22

some elements (Bhan et al., 1959). Examples of the effect of washing on corn leaf assays are given in Table 20-3.

B. Drying and Particle-Size Reduction

Drying should be rapid to minimize dry weight losses (Lockman, 1970), but at a temperature that will not cause the tissue to decompose. Corn and grain sorghum plant tissues can be easily oven dried at 80 °C in 48 h or less in a dust-free, forced-draft oven. The temperature should not exceed 85 °C because higher temperatures can result in significant thermal losses (Steyn, 1959). Tissue can also be dried in a microwave oven (Carlier & van Hee, 1971; Shuman & Rauzi, 1981) in about 10 min, although only small quantities of material can be dried at a time. Isaac and Johnson (1983) successfully microwave dried corn leaves prior to protein N assay by near infrared spectroscopy.

Reducing the dried tissue to a particle size suitable for laboratory analysis, and at the same time, ensuring a greater degree of homogeneity for the laboratory-prepared sample, is done either by the cutting action of a Wiley or hammer mill, by crushing in a ball mill, or by abrasion in a cyclone (UDY) mill. Most mills will contaminate the sample with particles of the contact surfaces, such as Cu and Zn from brass fittings, and even Fe from fittings or cutting and crushing surfaces made of steel. To avoid Fe contamination, tissue sample reduction must be done either by hand cutting or crushing in an agate ball mill. Grinding devices with Al, plastic (will add Na), or rubber (will add Zn) fittings are potential sources for contamination.

A Wiley mill fitted with a 20-mesh screen is commonly used for milling plant tissue. Particle-size reduction to <20 mesh is not necessary unless aliquots of <0.5 g are to be assayed in the laboratory. The finer the screen (40 or 60 mesh), the more homogeneous the milled sample will be, but finer grinding requires longer milling time. The longer contact time between the

tissue and mill surfaces increases the potential for contamination from the mill surfaces (Hood et al., 1944).

With most milling procedures, segregation of the finer particles is likely. This can be partially controlled by eliminating static electricity build-up and by carefully mixing the milled sample (Smith et al., 1968; Nelson & Boodley, 1965). Adherence of the finer plant particles to mill components can be partially overcome by a vacuum system attached to the mill (Graham, 1972), or by using pulsing air (Ulrich, 1984). When using a Wiley mill for milling corn and grain sorghum plant tissues, which are often fibrous and will easily segregate according to particle size, sufficient time should be allowed for the entire sample to pass through the mill. Ball or cyclone milling corn or grain sorghum leaf tissues will usually produce a more homogeneous laboratory sample than milling in a Wiley-type cutting mill.

C. Organic Matter Destruction

A more complete discussion on how best to destroy the plant tissue's organic matter content may be found in chapter 15 (Jones and Case). Either 8-h muffling at 500 °C followed by hot acid solution (Munter & Grande, 1981), or wet digestion in various mixtures of acids (Tolg, 1974), are possible methods for the destruction of organic matter in corn and grain sorghum plant tissues. Block digestion procedures, described by Zasoski and Burau (1977) and Havlin and Soltanpour (1980), have particular appeal when large numbers of samples are to be digested by wet oxidation. Books by Gorsuch (1970) and Bock (1978) are good references on methods used for organic matter destruction.

D. Laboratory Analysis

Advances in instrumental analytical chemistry since 1970 have had a great impact on methods suitable for the assay of plant tissue digests for their elemental contents. Traditional wet chemistry procedures described by Piper (1942), Jackson (1958); Johnson and Ulrich (1959), as well as flame emission and atomic absorption spectroscopy described by Isaac and Kerber (1971) and by the Technicon AutoAnalyzer² (manufactured by Technicon Corp., Tarrytown, NY 10591), an instrumental procedure for the determination of Ca, Mg, P, and K in plant tissue digests (Steckel & Flannery, 1971) are being superseded by more rapid analytical methods.

Emission spectroscopy has been and continues to be the method of choice for the elemental assay of plant tissue digests, using a progression of excitation sources from AC and DC arcs (Mitchell, 1964), to AC spark (Baker et al., 1964; Jones, 1976), and more recently to either inductively coupled plasma (Dalquist & Knoll, 1978; Munter & Grande, 1981; Soltanpour et al., 1982) or DC plasma (DeBolt, 1980). In many of today's plant analysis laboratories, elements in plant tissue digests, from trace to percent concentrations, are being easily and quickly determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Fassel & Kniseley, 1974; Scott et al.,

1974; Walsh, 1983; Montaser & Golightly, 1987). If the spectrometer is evacuated, S can also be determined. Today, analysts prefer using high-speed multi-element analyzers with computer or microprocessor control, requirements that are met by the ICP excitation spectrometer (Jones, 1984b).

X-ray emission spectroscopy (Alexander, 1965; Kubota & Lazar, 1971; Mudrock & Mudrock, 1977) is another technique applicable for the elemental assay of plant tissues. Although this technique of analysis is nondestructive, matrix effects have seriously hampered its acceptance and broad use.

Kjeldahl digestion, an analytical technique with more than 100-yr history (Morries, 1983), is the usual procedure for N determination. A standardized Kjeldahl procedure is described in the *AOAC Manual* (Williams, 1985), and a semi-automated procedure is given by Isaac and Johnson (1983). There is an excellent review article by Nelson and Sommers (1980) on the Kjeldahl method as well as a more recent one by Jones (1987).

Various procedures for the determination of S have been described by Beaton et al. (1968), and a turbimetric procedure using an AutoAnalyzer² (manufactured by Technicon Corp., Tarrytown, NY 10591) by Wall et al. (1980). The LECO Sulfur Analyzer² (manufactured by LECO Corp., St. Joseph, MI 49085-2396) procedure has been described by Jones and Isaac (1972), and more recently by Hern (1984).

III. INTERPRETATION OF ANALYSIS

A. Elemental Distribution in Plant

Most of the essential elements are not evenly distributed in the corn plant, nor does their concentration remain constant in any one plant part or section of the plant during its life cycle. The normal range in concentration for 14 elements is given in Table 20-4. Hanway (1962a) followed the uptake and distribution of N, P, and K in different parts of the corn plant during the growing season. He also followed their concentration in various plant parts (Hanway, 1962b). Benne et al. (1964) determined the composition of corn plants at different stages of growth and accumulation of essential elements in corn on a land area basis. Gorsline et al. (1965) followed the change in concentration and uptake of 11 elements in the leaves, stalks, tassels, and ears of corn plants from emergence to maturity. Clark (1975a, b) determined the concentrations of various elements in corn leaves and the whole plant with age. Similarly, Jones (1983) monitored N and P contents in corn and grain sorghum at growth stages defined by Vanderlip and Reeves (1972). Ohki (1975) found that critical Mn values varied considerably among the leaf blades of grain sorghum, increasing with increasing age (top vs. bottom leaves). All of these studies clearly show that element content varies among plant parts and will change within the same plant part with age. As was mentioned earlier,

²Trade name and company used to provide specific information and does not constitute endorsement by the authors.

Tabel 20-4. The normal expected range in element concentration for various parts of a corn plant.†

Average range in concentration					
Element	Whole plants at 3 to 4 leaf stage	Ear leaf at silk	Stalk in silk		Grain at maturity
			Above ear node	Below ear node	
<hr/> g kg ⁻¹ <hr/>					
N	35-50	27-35	--	--	10.0-25.0
P	4-8	2-4	1-2	1-2	2.0-6.0
K	35-50	17-25	10-20	20-30	2.0-4.0
Ca	9-16	4-10	1-3	1-3	0.1-0.2
Mg	3-8	2-4	1-3	1-3	0.9-2.0
S	2-3	1-3	--	--	--
<hr/> mg kg ⁻¹ <hr/>					
Al	100-200	10-200	10-25	50-100	--
B	7-25	4-15	4-12	4-9	1-10
Ba	--	0-50	5-20	2-15	--
Cu	7-20	3-15	3-15	3-10	1-5
Fe	50-300	50-200	50-75	50-100	30-50
Mn	50-160	20-250	20-70	50-100	5-15
Na	--	1-400	1-100	1-100	--
Sr	--	10-100	10-50	10-30	--

† Based on numerous analyses of corn plants collected by J.B. Jones and analyzed at the Ohio Plant Analysis Laboratory, Wooster, OH during the years 1965 to 1969.

certain elements will also be unevenly distributed within the corn leaf as is shown in Table 20-1.

These changing patterns of element concentration and distribution within the plant and among its specific parts emphasize the care required when collecting tissue for analysis. The heterogeneous nature of elemental content requires that specific sampling procedures be employed. Whole plant analyses, except for very young plants, are of limited value since the mixing of leaves, stalks, and other plant parts results in heterogeneous mixtures of questionable value.

Element uptake and dry matter production are not steady-state processes. Concentration and dilution occur due to differences between plant growth and element absorption as well as from the movement of the elements within and between plant parts (Bates, 1971). Terman and Noggle (1973) and Terman et al. (1977), to define the early growth rate-element concentration relationship, studied element concentration changes in corn as affected by dry matter accumulation with age and response to applied fertilizers. Under normal growing conditions, elemental absorption and plant growth parallel each other during most of the vegetative growth period. Exceptions occur only during the early growth period shortly after germination, and then after seed set and at the beginning of senescence. However, if the normal growth rate is interrupted, then elemental accumulation or dilution can occur (Jarrell & Beverly, 1981).

Although the concentrations of various elements in the corn plant can fluctuate considerably during the growing season, total uptake (concentration \times dry matter) of the whole plant plotted against time provides fairly smooth curves (Ritchie & Hanway, 1982; Al-Ansari, 1985). Most of the variations in elemental content are due to concentration or dilution effects associated with dry matter accumulation (Jarrell & Beverly, 1981). Therefore, it is essential that the time of sampling be known and considered when interpreting a plant analysis result.

B. Other Factors Affecting Interpretation

Two other important factors to consider when interpreting a plant analysis result are: (i) the influence of applied fertilizers and (ii) possible varietal effects on elemental composition. Bennett et al. (1953) correlated the N, P, and K content of the ear leaf and grain to yield at varying rates of N fertilization. They obtained a significant multiple regression of ear leaf N and P contents vs. grain yield. When the ear leaf N content was 2.8% or greater, no further increase in grain yield occurred. Similarly, Gallo et al. (1968) studied the relationship between leaf composition and grain yield.

Baker et al. (1966), from analyses of more than 50 000 corn leaf samples, reported that the elemental content of hybrids differed greatly, indicating that the level of accumulation of elements in the ear leaf was under partial genetic control. Munson (1969), Gorsline et al. (1968), and Ali and Johnson (1979) have shown that all corn plants do not absorb every element equally. This suggests inherited characteristics for element uptake. Rivard and Bandel (1974) reported that, although varietal differences in the concentrations of N, P, K, and Ca in field corn were statistically significant, those differences were not large enough to interfere with the interpretation of a plant analysis result. Recently, Russell and Pierre (1980) found a relationship between corn single crosses and their parent inbred lines for N content of grain. Kamprath et al. (1982) found a greater N use efficiency by an improved corn population than that by an unimproved one. Therefore, corn genotype may be an important factor in the interpretation of a plant analysis, requiring determination as to what effect genotype has on interpretative data, whether these data are critical values, sufficiency ranges, or DRIS norms.

C. Critical Values

Earlier methods for interpreting a plant analysis centered around single values, known as "critical" or "standard" values (Kenworthy, 1961). A critical value has been defined in numerous ways (Macy, 1936; Tyner, 1946; Ulrich, 1952; Gallo et al., 1968; Melsted et al., 1969), but essentially, it is that concentration correlated with a 10% yield decrease or that concentration where visual deficiency symptoms appear. Tyner (1946) published critical values for corn as 2.90% for N, 0.295% for P, and 1.30% for K; while Melsted et al. (1969) suggested 3.00% for N, 0.25% for P, 1.90% for K, 0.40% for Ca, and 0.25% for Mg. All these values were based on the assay

of the sixth leaf from the base of the plant at the time the plant was silking. Others have published critical values for several elements, giving values for various plant parts and times of sampling as shown in Table 20-5. As previously indicated, plant analysis data for grain sorghum is quite limited. It is also comparatively recent when compared to that available for corn. Most of the work in the USA has dealt with sufficiency ranges and DRIS norms. However, in Australia, Weir (1983) has determined critical values for macronutrients and most of the micronutrients in grain sorghum, and others in the USA and India have published critical values for some of the micronutrients (Table 20-5). Though of some use, critical values are significantly limited in that they only designate single points between elemental deficiency and sufficiency.

D. Sufficiency Ranges

If the full benefits of the plant analysis technique are to be realized, yield response curves as a function of element concentration must be established for all those elements that affect plant growth. These response curves are similar to those that have been described by Prevo^t and Ollangnier (1961) and Smith (1962) as shown in Fig. 20-1. Although, research has not been as extensive as that involving the determination of critical values, sufficient study has been done for most elements to describe the nature of the entire response curve which establishes the basis for setting the limits of the sufficiency range. The sufficiency range may be defined as that elemental concentration range between the critical value and when an excess or toxic concentration occurs. It may also be defined as that range in elemental concentration where no yield reduction occurs, nor nutrient element stress symptoms appear.

Element concentration sufficiency ranges for corn, published by Jones (1967), Neubert et al. (1969), Escano et al. (1981a, b) and Cornforth and Steele (1981), are given in Table 20-6. Ranges for grain sorghum published by Lockman (1972a, b) and Whitney (1970) are presented in Table 20-7. Some of the upper limits of these ranges may be based on partially known or inadequately defined response curves, leaving some question as to their reliability. However, these sufficiency ranges form the basis for the more commonly used procedure when interpreting a plant analysis result for corn and grain sorghum. It is important to remember that all of these interpretive ranges are designated for a particular plant part taken at a specified time and, therefore, cannot be applied to an assay result of a different plant part or from a different time of sampling. A compilation of interpretative ranges for corn and grain sorghum leaf analyses may be found in books by Chapman (1961), Reuther and Robinson (1986), and Martin-Prevel et al. (1987).

Researchers have emphasized the complexities that can be associated with an interpretation of corn leaf analysis. Dumenil (1961) and Hanway and Dumenil (1965) noted, for instance, that there is an interaction between N and P in corn leaves that affects the critical value of the one element depending on the concentration of the other. Jones (1963) observed changes

Table 20-5. Published critical values for elements found in various corn and grain sorghum plant tissues.

Element	Time	Plant part	Critical value	Reference
<u>Corn, g kg⁻¹</u>				
N	Not given	Not given	7.0	Goodall & Gregory, 1974
	At tassel	Ear leaf	30.0	Melsted et al., 1969
	At tassel	Leaves	29.0	Gallo et al., 1968
	At silk	Sixth leaf from base	29.0	Tyner, 1946
	40-60 cm ht.	Entire plant	25.6	Rehm et al., 1983
	At silk	Second leaf below ear	22.5	Rehm et al., 1983
P	8 wk	Whole plant top	1.4	Terman et al., 1972
	Late summer	Lower stems	0.044	Goodall & Gregory, 1947
	At tassel	Leaves	23.0	Gallo et al., 1968
	At silk	Sixth leaf from base	2.95	Tyner, 1946
	At tassel	Ear leaf	2.5	Melsted et al., 1969
K	Late summer	Lower stems	0.83	Goodall & Gregory, 1947
	At tassel	Ear leaf	19.0	Melsted et al., 1969
	At tassel	Leaves	17-27	Gallo et al., 1968
	At silk	Sixth leaf from base	13.0	Tyner, 1946
	At silk	Leaf opposite and just below ear shoot	20.0	Hanway, 1962
	Ca	At tassel	Ear leaf	4.0
Mg	At tassel	Ear leaf	2.5	Melsted et al., 1969
			1.5	Peaslee & Moss, 1966
<u>Corn, mg kg⁻¹</u>				
B	At tassel	Ear leaf	10.0	Melsted et al., 1969
	Not given	Upper leaves	12.2	Berger et al., 1957
	5+ wk	Entire plant	1.8	Makarim & Cox, 1983
Cu	At tassel	Ear leaf	5.0	Melsted et al., 1969
Fe	At tassel	Ear leaf	15.0	Melsted et al., 1969
Mn	At tassel	Ear leaf	15.0	Melsted et al., 1969
Mo	Not given	Stems	0.11	Dios & Broyer, 1965
	Not given	Entire plant	0.10	Peterson & Purvis, 1961
Zn	5 wk	Entire plant	1.8	Makarim & Cox, 1983
	At tassel	Ear leaf	15.0	Melsted et al., 1969
	At tassel	Ear leaf	17.2	de L. Beyers & Coetzer, 1969
	At tassel	Leaf at second node below ear	15.0	Veits, 1953
	At silk	Second leaf below ear	14.9	Grunes et al., 1961
<u>Grain sorghum, g kg⁻¹</u>				
N	Full heading	Second blade below apex	25.0	Weir, 1983
P	Full heading	Second blade below apex	2.5	Weir, 1983
K	Full heading	Second blade below apex	18.0	Weir, 1983
S	Full heading	Second blade below apex	1.5	Weir, 1983

(continued on next page)

Table 20-5. Continued.

Element	Time	Plant part	Critical value	Reference
<u>Grain sorghum, g kg⁻¹</u>				
Ca	Full heading	Second blade below apex	2.0	Weir, 1983
Mg	Full heading	Second blade below apex	1.5	Weir, 1983
Cl	After head emergence	Fourth blade below flag leaf	<7.1	Francois et al., 1984
<u>Grain sorghum, mg kg⁻¹</u>				
Cu	30 d after seeding	Middle blades	3.6	Agarwala & Sharma, 1979
Zn	Stage 3†	Youngest mature blade	10.0	Ohki, 1984
	49 d after seeding	Middle blades	20.0	Agarwala & Sharma, 1979
	Full flowering	Second blade below apex	18	Weir, 1983
Mn	Stage 5† (boot)	Flag leaf	10	Ohki, 1975
	Stage 5† (boot)	Second leaf below flag leaf	15	Ohki, 1975
Fe	35 d after seeding	Whole shoot	65	de Boer & Reisenauer, 1973
B	35 d after seeding	Middle blades	10	Agarwala & Sharma, 1979
	Full heading	Second blade below apex	5	Weir, 1983

† See Vanderlip and Reeves (1972).

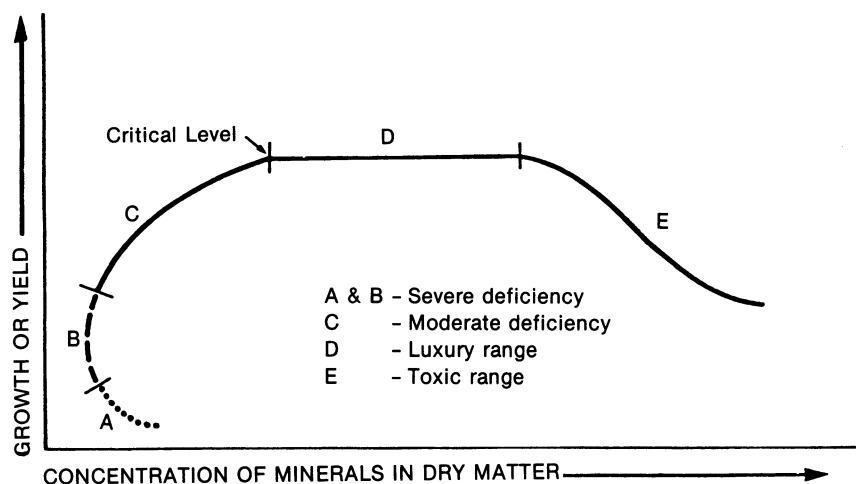


Fig. 20-1. General relationship between plant growth or yield and elemental content of the plant (Smith, 1962).

Table 20-6. Nutrient sufficiency ranges for corn ear leaf taken at silk as given by several workers.

Element	Jones (1967)	Neubert et al. (1969)	Cornforth and Steele (1981)		Escano et al. (1981a)
			g kg^{-1}		
N	27.6–35.0	26.0–40.0	22.5–33.0		21.0–36.0
P	2.5–4.0	2.5–5.0	1.8–3.2		2.6–3.5
K	17.1–25.0	17.0–30.0	17.0–30.0		17.0–23.0
Ca	2.1–10.0	2.1–10.0	4.0–8.0		3.5–4.9
Mg	2.1–6.0	3.1–5.0	1.3–2.5		1.7–3.0
S	--	2.1–5.0	1.2–3.0		1.5–2.3
mg kg^{-1}					
Al	200	--	--		200
B	4–25	15–90	4–25		--
Cu	6–20	8–20	8–20		13–19
Fe	21–250	21–250	--		70–120
Mn	20–150	34–200	18–140		32–170
Mo	--	0.6–1.0	--		--
Zn	20–70	50–150	22–85		32–52

in the elemental content of the ear leaf with increasing rates of N, P, and K fertilization as did Al-Ansari (1985) with different soil levels of available P and K. In a nutrient culture study, Clark (1970) found wide variance in the elemental content of the corn plant as various elements became deficient or excessive. Loue (1987) evaluated the equilibrium relationship that exists among Ca, Mg, and K in corn leaves. The importance of these interactions as they relate to yield has been reported by Peck et al. (1969), Walker et al.

Table 20-7. Nutrient sufficiency ranges for grain sorghum at several stages of growth.

Element	Lockman (1972a, b)				
	Whole plant, 23-39 d after planting	Youngest fully developed leaf 37-56 d after planting	Bloom stage third leaf below head 66-70 d after planting	Dough stage third leaf below head, 82-97 d after planting	Whitney (1970) Last fully extended leaves
	g kg ⁻¹				
N	35.0-40.0	32.0-42.0	33.0-40.0	30.0-40.0	30.0-50.0
P	3.0-6.0	2.0-6.0	2.0-3.5	1.5-2.5	2.5-4.0
K	30.0-45.0	20.0-30.0	14.0-17.0	10.0-15.0	27.5-40.0
Ca	9.0-13.0	1.5-9.0	3.0-6.0	2.0-6.0	--
Mg	3.5-5.0	2.0-5.0	2.0-5.0	1.0-5.0	--
mg kg ⁻¹					
B	1-13	1-10	1-10	1-6	--
Cu	8-15	2-15	2-7	1-3	5-15
Fe	160-250	55-200	65-100	40-80	--
Mn	40-150	6-100	8-190	8-80	--
Zn	30-60	20-40	15-30	7-16	15-40

(1971), and Walker and Peck (1972, 1974). Until recently when the DRIS concept was introduced, little had been done to incorporate these interactions into the interpretation of plant analysis data.

E. Diagnosis and Recommendation Integrated System

Diagnosing plant nutrient disorders using a critical value or sufficiency range requires that the elemental concentration result be compared with a standard value for that same tissue taken at that specified stage of growth. Because element concentrations vary depending on plant part, growth stage, genotype and geographic location, this approach has recognized limitations. A new concept for plant analysis interpretation has been proposed by Beaufils (1971, 1973) as a means to overcome some of these difficulties. The DRIS approach was designed to: (i) provide a valid diagnosis irrespective of plant age or tissue origin, (ii) rank nutrients in their limiting order, and (iii) stress the importance of nutrient balance.

DRIS is a unique approach that uses the principle of elemental inter-relationships by determining, in descending order, the elements that are most limiting. Beaufils used the survey approach by using the world's published literature and plotting elemental leaf content vs. yield, a distribution that is normally skewed. To normalize the distribution curve, the yield component is divided into low- and high-yield groups. Walworth et al. (1986) suggested that the data bank for determining DRIS norms have at least several thousand entries, be randomly selected, and that at least 10% of the population be in the high-yield subgroup. It is also important that the cutoff value used to divide the low- from the high-yielding subgroups be such that the high-yield data subgroup remains normally distributed. Selecting the elemental content mean, the ratio and product of elemental means are determined. The ratio or product selected for DRIS calculations is the one with the largest variance which in turn maximizes the diagnostic sensitivity.

The means and coefficients of variation (CVs) for DRIS reference parameters in high-yielding subpopulations are used in a special calibration formula described by Beaufils (1973). The calibration formula calculates relative indices for nutrients that range from negative to positive values depending on whether elements are relatively insufficient or excessive with respect to each other with the sum of all the indices always being zero. The more negative the index value for an element, the more limiting it is. When all the elements are available at similar concentrations to those found in the desirable populations, the DRIS index for each element approaches zero. Sumner (1977a, b, 1979, 1981) has discussed the DRIS system in considerable detail, including its application to corn. In addition, Walworth and Sumner (1987) have published an excellent review paper on DRIS.

The first list of DRIS diagnostic norms for 11 elements in corn leaves was published by Elwali et al. (1985a, b) and they are given in Table 20-8. A major premise of the DRIS system is the universal applicability of DRIS norms regardless of genotype, age of crop at sampling and plant location. However, Escano et al. (1981a, b), and Cornforth and Steele (1981), each

Table 20-8. The Diagnosis and Recommendation Integrated System (DRIS) foliar diagnostic reference norms for corn† (Elwali et al., 1985b).

Parameter	No.	Mean	SD	Parameter	No.	Mean	SD
N/P‡	1909	9.035	2.136	10N/Zn	1526	11.797	4.459
NK	1908	1.463	0.426	Zn/10P	1527	0.883	0.420
P/K	1909	0.169	0.054	Zn/10K	1526	0.140	0.068
Ca/N	1553	0.160	0.057	10Ca/Zn	1524	1.919	1.087
Ca/P	1554	1.447	0.612	10Mg/Zn	1527	0.830	0.504
Ca/K	1553	0.237	0.122	10S/Zn	760	0.952	0.365
Mg/N	1556	0.071	0.029	Fe/Zn	1268	4.464	1.837
Mg/P	1557	0.639	0.330	Mn/Zn	1520	1.716	1.175
Mg/K	1556	0.104	0.063	Cu/10N	1401	0.031	0.013
Mg/Ca	1554	0.465	0.182	Cu/10P	1402	0.277	0.140
S/N	788	0.084	0.019	Cu/10K	1401	0.045	0.022
S/P	788	0.703	0.225	10Ca/Cu	1402	6.022	3.511
S/K	787	0.114	0.029	10Mg/Cu	1402	2.768	1.935
Ca/S	785	1.978	0.893	Cu/10S	664	0.375	0.211
S/Mg	788	1.195	0.395	Cu/Fe	1236	0.079	0.036
Fe/10N	1297	0.394	0.097	Cu/Mn	1395	0.260	0.174
Fe/10P	1298	3.588	1.177	Cu/Zn	1372	0.356	0.200
Fe/10K	1297	0.568	0.201	B/10N	402	0.024	0.012
10Ca/Fe	1298	0.410	0.189	B/10P	403	0.269	0.135
10Mg/Fe	1298	0.190	0.098	B/10K	402	0.043	0.033
Fe/10S	687	4.868	1.419	B/10Ca	403	0.153	0.076
Mn/10N	1459	0.151	0.087	B/10Mg	403	0.335	0.152
Mn/10P	1550	1.416	1.063	10S/B	112	3.185	1.039
Mn/10K	1549	0.218	0.140	B/Fe	389	0.068	0.036
Mn/10Ca	1547	1.048	0.676	B/Mn	399	0.173	0.150
Mn/10Mg	1550	2.485	1.780	B/Zn	410	0.265	0.134
10S/Mn	782	0.648	0.351	B/Cu	401	0.950	0.620
Mn/Fe	1293	0.405	0.249				

† Number of observations, means, and standard deviations (SD) of DRIS reference parameters in the subpopulation yielding >10.0 Mg of grain ha^{-1} .

‡ Nutrient concentrations were expressed in g kg^{-1} for N, P, K, Ca, Mg, and S and in mg kg^{-1} for Fe, Mn, Zn, Cu, and B.

using small databases, concluded that local calibration improves the accuracy of a DRIS diagnosis. Elwali et al. (1985a) also noted that biological estimates of this type can only be considered, at best, approximations based on the extent of available data with modification and refinement coming in time. Walworth and Sumner (1987) also published DRIS norms for corn from six different databases. They cautioned on universal use of DRIS norms derived from but one geographical area, stating that the CVs may not reflect the extent of normal variation in all geographical areas. They concluded that by pooling databases covering most geographic areas, derived DRIS norms should be applicable to a range of specific locales and conditions.

Kelling and Schulte (1986) have found the DRIS system for interpreting corn leaf analysis a supplement rather than a substitute for the sufficiency range concept when evaluating farmer received samples at the Wisconsin Soil Testing and Plant Analysis Laboratory.

Arogun (1978) derived DRIS norms for grain sorghum on the basis of a data bank comprised of 907 sets of observations of leaf analyses and yield. The data bank was developed from the literature and unpublished results

Table 20-9. Chemical analysis for the high-yielding subpopulation of sorghum crops and resulting norms selected for DRIS indices† (Arogun, 1978).

Element	Mean	CV	Parameter	Mean	CV
	g kg ⁻¹	%			%
N	30.3	17	P/N	0.112	19
P	3.4	15	N/K	2.355	23
K	13.1	11	P/K	0.259	21
Ca	4.4	20	N/Ca	7.20	30
Mg	2.4	24	P/Ca	0.795	31
			K/Ca	3.080	24
			Mg/N	0.079	26
			P/Mg	1.518	45
			Mg/K	0.183	26
			Mg/Ca	0.553	30

† Means and coefficients of variation in the subpopulation (135 of 907 crops) yielding > 7.1 Mg of grain ha⁻¹.

supplied by several researchers, with most of the analysis data originating from experimental plots located in Kansas. Using average analyses for high- (> 7100 kg of grain ha⁻¹) and low- (< 7100 kg of grain ha⁻¹) yielding populations of sorghum crops, he calculated and selected foliar diagnostic reference norms shown in Table 20-9. The formulae for calculation of DRIS indices for grain sorghum are as follows:

$$\text{N index} = \frac{-f(\text{P/N}) + f(\text{N/K}) + f(\text{N/Ca}) - f(\text{Mg/N})}{4} \quad [1]$$

$$\text{P index} = \frac{f(\text{P/N}) + f(\text{P/K}) + f(\text{P/Ca}) + f(\text{P/Mg})}{4} \quad [2]$$

$$\text{K index} = \frac{-f(\text{N/K}) - f(\text{P/K}) + f(\text{K/Ca}) - f(\text{Mg/K})}{4} \quad [3]$$

$$\text{Ca index} = \frac{f(\text{N/Ca}) + f(\text{P/Ca}) + f(\text{K/Ca}) + f(\text{Mg/Ca})}{4} \quad [4]$$

$$\text{Mg index} = \frac{f(\text{Mg/N}) - f(\text{P/Mg}) + f(\text{Mg/K}) + f(\text{Mg/Ca})}{4} \quad [5]$$

in which $f(\text{P/N}) = \left[\frac{\text{P/N}}{\text{p/n}} - 1 \right] \frac{1000}{\text{CV}}$ when $\text{P/N} > \text{p/n}$

or $f(\text{P/N}) = 1 - \left[\frac{\text{p/n}}{\text{P/N}} \right] \frac{1000}{\text{CV}}$ when $\text{P/N} < \text{p/n}$

where P/N is the ratio of $P\%$ and $N\%$ in the tissue under diagnosis and p/n is the value of the corresponding norm for the high-yielding population and CV is the corresponding CV . The other functions are calculated in a similar manner.

Tissue concentrations of N , P , K , Ca , and Mg were used to derive the norms, and Arogun (1978) tested them with sorghum plants grown in a greenhouse experiment. Sumner et al. (1983) further tested Arogun's DRIS norms on field data obtained by Reneau et al. (1983), finding them valid and usable for diagnostic purposes.

IV. PRACTICAL APPLICATION AND FUTURE POTENTIAL

In the USA, some 500 000 plant tissue samples (Jones, 1985) are analyzed yearly for farmers by both state-sponsored and commercial laboratories. To some people, this indicates a significant under-utilization since about four million soil samples are analyzed for farmers each year in these same laboratories. To most farmers, plant analysis use is still primarily viewed as a diagnostic device to determine the source of a suspected nutrient element insufficiency. And yet its most useful application is as a means of evaluating the soil/plant nutrient element status, a use first suggested by Krantz et al. (1948), and more recently put into a systems approach by Jones (1986). Without a plant analysis result, the farmer is not able to adequately evaluate whether all the essential elements, as well as several nonessential elements that can affect plant growth, are at satisfactory levels in the plant. Environmentally, a plant analysis can provide the means of assessing heavy metal contents of plants when waste products (animal manure, sewage sludge, and industrial wastes) have been or are being soil applied, warning of possible excesses or imbalances that can either reduce yields or adversely affect product quality or safety (Logan & Chaney, 1983; Adriano, 1986).

Yearly plant analysis results can also be "tracked" as has been discussed by Clements (1960) for sugarcane (*Saccharum officinarum* L.) and by Jones et al. (1980) for peanut (*Arachis hypogaea* L.). As shifts in nutrient element concentrations are observed as moving out of the sufficiency range, changes in crop production practices can be made before yield-affecting insufficiencies occur. Repeated plant analyses can also serve as a means of evaluating the effects of mineral cycling on the elemental content of the plants as crop residues are returned to the soil. Tracking requires systematic and standardized sampling and analysis procedures along with the appropriate sufficiency ranges for the elements being tracked. With experience, the farmer will be able to customize this system of plant analysis used to fit his own individual soil/plant management situation, thereby minimizing yield losses due to nutrient element insufficiencies. Regardless of how a plant analysis result is to be used and interpreted, knowledge of those factors affecting nutrient availability and uptake by plants is also required if the course of action to correct a plant nutritional problem is to be effective (Barber, 1984).

With recent significant analytical advancements now providing fast and low-cost plant analysis service, and the current sufficiency of interpretative data, farmers should be assaying their crops on a regular basis, combining the results of soil tests and plant analyses to assess the nutrient element status of their soil/crop system (Jones, 1986).

V. TISSUE TESTING

Although the terms *tissue testing* and *plant analysis* have sometimes been used interchangeably, they denote two different techniques. Plant analysis normally denotes a total analysis performed in the laboratory, using methods and procedures discussed in some detail in this chapter, while tissue testing denotes a semiquantitative quick test on plant sap extracted from fresh tissue, and normally performed in the field. Since there has been and continues to be considerable interest in tissue testing for corn, a brief description of the technique and its application deserves some attention.

Much of the early tissue testing research was done between the mid-1920s and early 1950s. The tests using extracted sap are mostly colorimetric methods with developed color intensity being compared with standard color charts serving as the means of interpretation. Although the testing procedures are relatively simple, the results obtained are frequently not easy to evaluate. With practice, however, this system of testing can be used effectively. The user must work with plants of known nutrient status to develop the proper sampling, chemical test procedures, and interpretation skill required. It is important that only fresh reagents and test papers be used at all times.

Krantz et al. (1948) were the first to describe field-testing procedures for corn. Using sap pressed from fresh tissue, they gave instructions for the semiquantitative determination of NO_3 , PO_4 , and K employing test papers, vials, reagents, and color charts. Wickstrom (1967) also has discussed the use of tissue tests as a means for field diagnosis of corn plant nutrient status. Syltie et al. (1972) have given procedural details for conducting tissue tests in the field for the elements N, P, K, Mg, and Mn. Instructions for the preparation of reagents and techniques for conducting the tests are also included. Scaife and Stevens (1983) have found "Merckoquant" test strips suitable for NO_3 determination in the field as a means of assessing the N status of vegetable crops. This method could be applied to corn tissue.

The relationship between the $\text{NO}_3\text{-N}$ content of basal corn stems and grain yield has been evaluated, but research is limited and critical stem $\text{NO}_3\text{-N}$ contents for given levels of grain yield have not been well established. Rauschkolb et al. (1974) found 0.40 to 0.60% $\text{NO}_3\text{-N}$ (dry wt. basis) adequate for maximizing yields. Iversen et al. (1985) found the critical stem $\text{NO}_3\text{-N}$ content for corn varied from 1.10 to 1.60%, and they found significant differences between plants with adequate and deficient levels of stem $\text{NO}_3\text{-N}$ for maximum yields as early as the V-5 growth stage. McClenahan and Killorn (1988) used 5-cm stem segments immediately above the soil surface at the V-6 growth stage (Hanway, 1982) for $\text{NO}_3\text{-N}$ determinations and

found critical levels of 0.90 and 1.78% (dry wt. basis) for maximum yields on soils derived from loess and glacial till, respectively. Although further calibration data are needed, this procedure would permit detection of N needs early enough during the growing season to permit necessary applications of fertilizer N.

Iron can be determined by a tissue test conducted in the field, a procedure developed by Bar-Akiva et al. (1978) and later modified by Bar-Akiva (1984). Peroxidase activity is measured by floating leaf discs in a reactive solution with the development of a blue color indicating an adequate Fe status in the plant tissue. Many believe that only this type of test, or ones similar to it, can satisfactorily determine the Fe status of a plant (Chaney, 1984).

Compared to a laboratory conducted plant analysis, field-conducted tissue tests cost less and provide immediate results, therefore, some see this as a distinct advantage for tissue tests in preference to a plant analysis. It should be remembered, however, that most tissue tests are not entirely quantitative. Rather, they provide the tester with a qualitative "yes" or "no" evaluation of the crop; that is, the element being evaluated is either present or not present at a particular concentration. It takes considerable practical experience and repeated observations to feel confident when making interpretations based on a tissue test result. To some, the tissue test and its interpretation is considered an acquired "art" rather than a strict quantitative analytical procedure. Although the test procedures themselves are based on sound analytical chemistry, it is their utilization and interpretation that requires skill gained only by repeated practical experience.

Quick tests of soil and plant tissue conducted in the field combined with field observations have been coined "The Diagnostic Approach," a procedure of observation, testing, and evaluation discussed in a special issue of *Better Crops With Plant Food* published in 1984 (published by the Potash and Phosphate Institute, Atlanta, GA).

VI. SUMMARY

Corn and grain sorghum plants have been found to contain similar amounts of most elements. Since the data for grain sorghum is scant, the two crops can be treated similarly unless specific data are available that distinguish between them. Although, to farmers, the primary use for a plant analysis is still to diagnose suspected essential element deficiencies, they need to see its broader application and to use it in a systems approach to maintain their soil/crop nutrient element status within an established sufficiency range. While plant analysis is not the total answer to detecting and solving all nutritional disorders in corn and grain sorghum plantings, it is a better tool now than it was in previous years. For a plant analysis result to be meaningful, it must be analytically correct, therefore, the care required to select, prepare, and analyze the gathered tissue sample. There have been considerable advances made on how best to prepare samples for analysis and significant technological advancements in analytical equipment used to assay plant tissue digests.

The "critical level" and "sufficiency range" concepts are generally satisfactory for the interpretation of a plant analysis result, but they are limited to a particular plant part taken at a specified time. Even with plant part and age defined, concentrations can be affected by interactions among elements and may be different for various genotypes, thus necessitating consideration of factors other than simple critical levels or sufficiency ranges. Therefore, the interpreter must be knowledgeable and experienced.

DRIS is a new unique approach for the interpretation of a plant analysis result that applies the principle of elemental interrelationships as a means for determining by order elements most limiting. The DRIS concept of interpretation is based on the balance among elements rather than specific levels of elements. Essentially, elemental balances (in the form of indices) within the tissue under diagnosis are compared with norms calculated from large data banks of analysis results vs. yield. This approach reportedly lessens or negates consideration of plant part, age, and genotype when interpreting a plant analysis result. Data banks of analyses from plants in "high-yielding populations" must be available and the tissue under diagnosis must be analyzed for two or more elements for the DRIS system to apply. Calculation of results can be cumbersome, but this can be overcome by the use of computer programs. From practical experience, a combination of DRIS and sufficiency range procedures seems to provide the most useful approach for the interpretation of a plant analysis result at the present time.

Tissue tests, consisting of rapid semiquantitative determinations, can be valuable when a quick diagnosis in the field is required. However, effective utilization and interpretation does require considerable skill on the part of the user.

Improvements continue to be made in all aspects of the plant analysis and tissue testing techniques with particular research interest on the effect genotype has on nutrient element requirement and efficiency of utilization. Further advances in the DRIS approach to interpretation will no doubt be made. Future research will probably lead to nutrient diagnosis at the cellular level by in situ monitoring of element concentrations.

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